THE UNIVERSITY
OF ILLINOIS
LIBRARY
630.1606
AS
v. 3
Cop. 3

UNIVERSITY OF ILLINOIS
LIBRARY-CHEMISTRY

JOURNAL

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

UNIVERSITY OF ILLINOIS
LIBRARY-CHEMISTRY

BOARD OF EDITORS

C. L. Alsberg, Chairman

R. E. Doolittle — C. B. Lipman
E. F. Ladd — L. L. Van Slyke

N. A. Parkinson, Associate Editor

VOLUME III

1917-20

1920
ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS
BOX 744, ELEVENTH STREET STATION,
WASHINGTON, D. C.

UNIVERSITY OF ILLINOIS
LIBRARY-CHEMISTRY

COPYRIGHT, 1920
BY
JOURNAL OF THE ASSOCIATION OF OFFICIAL
AGRICULTURAL CHEMISTS

630.1606
AS
v.3
Cop.3

LIBRARY
UNIVERSITY OF ILLINOIS
URBANA

CONTENTS

PROCEEDINGS OF THE THIRTY-SECOND ANNUAL CONVENTION, NOVEMBER, 1915.

MONDAY—AFTERNOON SESSION. PAGE

Report on Canned Vegetables. By W. D. Bigelow 1
Report on Tea and Coffee. By J. M. Bartlett 21
Determination of Saccharin in Foods. By C. B. Gnadinger 25
Report on Preservatives. By A. F. Seeker 33
Report on Heavy Metals in Foods. By E. L. P. Treuthardt 43

TUESDAY—MORNING SESSION.

Report on the Separation of Nitrogenous Bodies (Milk and Cheese). By A. W. Bosworth 53
Report of Secretary-Treasurer. By C. L. Alsberg 54
Report on Journal of Association of Official Agricultural Chemists. By C. L. Alsberg 55
Report of Committee A on Recommendations of Referees. By W. W. Skinner 59

TUESDAY—AFTERNOON SESSION.

Report of Committee B on Recommendations of Referees. By R. E. Stallings 66
Report of Committee C on Recommendations of Referees. By H. E. Barnard 72
Report of Committee on Editing Methods of Analysis. By R. E. Doolittle 89

WEDNESDAY—MORNING SESSION.

Report on Phosphoric Acid. By L. S. Walker 90
Report on Use of Citrates in Determination of Phosphoric Acid. By W. J. Jones, jr. 97
Preparation of Organic Material for Determination of Phosphoric Acid and Potash in Aliquots of Same Solution. By R. M. West 99
New Method for Drying Ether and Sample in Determination of Ether Extract. By R. M. West 101
Report of the Committee on Availability of Phosphoric Acid in Basic Slag. By C. B. Williams 104
Report on Availability of Potash. By E. E. Vanatta 105
Report on Determination of Potash. By T. D. Jarrell 107
Report on Soils. By J. W. Ames 121
Lime Requirements of Some Acid Soils. By S. D. Conner 139
Determination of Lime Requirements of Soils by Use of Calcium Bicarbonate. By L. P. Howard 141
Status of the Problem of Lime Requirement. By W. H. McIntire 144
Determination of Phosphorus in Soils. By H. A. Noyes 149
Study of Soil Containing Residual Limestone. By H. A. Noyes 151
Report on Inorganic Plant Constituents. By A. J. Patten 153
Report on Insecticides. By R. C. Roark 157

WEDNESDAY—AFTERNOON SESSION.

Report of Committee on Nominations. By W. B. Ellett 187
Report of Committee on Resolutions. By R. J. Davidson 187
Report of Committee of Review on the Analysis of Lime Sulphur Solutions. By R. J. Davidson 188
Report on Alkaloids. By H. C. Fuller 188
Delicate Test for Strychnin. By H. E. Buc 193
Preliminary Study of Some of the Physical and Chemical Constants of Balsam Peru. By E. C. Merrill 194
Report of Committee to Cooperate with Other Committees on Food Definitions and Standards. By William Frear 198
Inorganic Phosphorus in Animal Tissue. By F. M. Beegle 204
Report on Nitrogen. By R. N. Brackett and H. D. Haskins 207
Symposium on Determination of Nitrogen in Fertilizers. By P. F. Trowbridge 217
Investigations of the Kjeldahl Method for the Determination of Nitrogen. By I. K. Phelps and H. W. Daudt 218
Notes on Use of Potassium Permanganate in Determining Nitrogen by the Kjeldahl Method. By William Frear, Walter Thomas and H. D. Edmiston 220
Report on Testing Chemical Reagents. By C. O. Ewing 225

474587

PROCEEDINGS OF THE THIRTY-THIRD ANNUAL CONVENTION, NOVEMBER, 1916.

PAGE

Officers, Referees, Associate Referees and Committees of the Association of Official Agricultural Chemists, for the Year Ending November, 1917 228
Members and Visitors Present 231
President's Address. By R. N. Brackett 238

MONDAY—MORNING SESSION.

Report on Dairy Products. By Harry Klueter 254
Report on Foods and Feeding Stuffs. By A. C. Summers 254
Report on Feed Adulteration. By Carleton Cutler 255
Report on Crude Fiber. By C. K. Francis 256
Report on Sugar. By C. A. Browne 261
Recommendations on Sugar. By W. D. Horne 263
Water in Foods and Feeding Stuffs. By W. J. McGee 264
Inorganic Phosphorus in Animal Tissue. By E. B. Forbes 264
Report on the Separation of Nitrogenous Substances in Milk and Cheese. By L. S. Palmer 273
Origin of the Neutralization Precipitate of Cows' Milk. By L. S. Palmer 274
Progress Report on the Separation of Nitrogenous Substances in Meat Products. By P. F. Trowbridge 275
Report on Testing Chemical Reagents. By C. O. Ewing 276

MONDAY—AFTERNOON SESSION.

Report on Phosphoric Acid. By W. J. Jones, jr. 279
Report on Phosphoric Acid in Basic Slag. By C. S. Lykes 286
Report on Nitrogen. By H. D. Haskins 289
Report on Nitrogen Determination. By R. B. Deemer 299
Substitution of Sodium Sulphate for Potassium Sulphate in the Kjeldahl-Gunning-Arnold Method for the Determination of Ammonia in Fertilizers. By T. D. Jarrell 304
Investigations of the Kjeldahl Method for Determining Nitrogen. By I. K. Phelps 306
Report on Potash. By T. D. Jarrell 315
The Separation and Gravimetric Estimation of Potassium. By S. B. Kuzirian ... 321
A Study of the Availability of Potash in Commercial Wood Ashes. By R. E. Rose 323
Nitrogenous Compounds in Soils. By C. B. Lipman 326
Report on Inorganic Plant Constituents. By A. J. Patten 329
Report on Insecticides. By R. C. Roark 331
The Occurrence and Determination of As^{III} and As^{V} in the Presence of Each Other in Arsenical Insecticides. By R. C. Roark 358
Report on Water. By W. W. Skinner 368
Report on the Lime Requirement of Soils. By F. P. Veitch 371
Report on Synthetic Products. By W. O. Emery 374
Report on Alkaloids. By H. C. Fuller 379
Report on Medicinal Plants. By Arno Viehoever 381
Report on Papain. By V. K. Chesnut 387

TUESDAY—MORNING SESSION.

Report on Food Adulteration. By Julius Hortvet 398
Report on Colors. By W. E. Mathewson 400
Tartrazine. By A. M. Doyle 402
Report on Fruit Products. By P. B. Dunbar and H. A. Lepper 402
Report on Wine. By B. G. Hartmann 409
Titration of Acidity in Colored Solutions. By B. G. Hartmann 410
The Isolation and Identification of Glycerol in Cider Vinegar. By R. W. Balcom and E. G. Grab 411
A Note on the Calculation of the Volume of a Liquid from Weight and Specific Gravity. By R. W. Balcom 413
Report on Flavoring Extracts. By A. E. Paul 415
Address. By C. S. Vrooman 418
Honorary President's Address. By H. W. Wiley 420

TUESDAY—AFTERNOON SESSION.

PAGE

Report on Spices. By H. E. Sindall 427
Report on Baking Powder. By H. E. Patten 429
Report on Fats and Oils. By R. H. Kerr 432
Report on Dairy Products. By Julius Hortvet 436
Report on Cereal Products. By J. A. Le Clerc 446
Report on Canned Vegetables. By W. D. Bigelow 453
Report on Cocoa and Cocoa Products. By Eugene Bloomberg 486
Report on Tea and Coffee. By H. M. Loomis 498
Report on Preservatives. By A. F. Seeker 504
Report on Metals in Food. By David Klein 512

WEDNESDAY—MORNING SESSION.

Report of Committee A on Recommendations of Referees and Revision of Methods. By W. W. Skinner 519
Report of Committee B on Recommendations of Referees and Revision of Methods. By R. E. Stallings 524
Report of Committee C on Recommendations of Referees and Revision of Methods. By H. E. Barnard 528
Report of Committee on Editing Methods of Analysis. By R. E. Doolittle 537

WEDNESDAY—AFTERNOON SESSION.

Report of Secretary-Treasurer. By C. L. Alsberg 576
Report on The Journal. By C. L. Alsberg 578
Report of Committee to Cooperate with Other Committees on Food Definitions and Standards. By William Frear 580
Report of Committee on Availability of Phosphoric Acid in Basic Slag. By C. B. Williams 585
Report of Committee on Amendments to Constitution and By-laws. By B. B. Ross 586
Report of Committee on Nominations. By C. C. McDonnell 589
Report of Committee on Resolutions. By William Frear 589
Obituary on Robert James Davidson. By W. B. Ellett 591
Obituary on Eugene Woldemar Hilgard. By C. B. Lipman 592
Obituary on George Edward Patrick. By William Frear 596
Obituary on Thomas Cuthbert Trescot. By William Frear 598

MONDAY—AFTERNOON SESSION.

REPORT ON CANNED VEGETABLES.

By W. D. Bigelow (National Canners' Association, Washington, D. C.),
Associate Referee.

Judging by the reports of previous referees, it seems that there is not a well-defined idea in the minds of the food chemists of the association regarding what can best be included in the group called "canned vegetables." The methods which have been adopted provisionally give evidence that in the minds of some this chapter is intended to include ketchup, which is rarely placed in cans, and pickles, which could scarcely be processed without softening. The methods that have been adopted provisionally consist almost entirely of certain analytical determinations, such as acidity, preservatives, coloring matter, and heavy metals. Some of these are commonly made with canned foods and some are not. None of them is peculiar to canned foods, and all of them might better be classed under general methods. As far as analytical determinations are concerned, canned foods do not differ from fresh foods or foods preserved by refrigeration or by drying. It is believed that this subject will be in all ways more satisfactory if attention be given to the development of methods which are especially applicable to the examination of canned foods. Some of these methods are bacteriological and probably do not come within the scope of the association. Others are of a character which bring into play individual opinion and personal equation. Such methods are difficult to define, and it is often impossible to state quantitatively the results obtained by them. Methods of this character are recognized in the trade and are used by buyers and sellers in defining grades of various canned products. They are also used by canners and manufacturers of cans and of canning machinery in fixing responsibility for spoilage. Such methods are not well formulated, and in their application more or less difference of opinion sometimes develops between men conversant with them. At the same time there is sufficient uniformity to make the methods of great value, and contracts of sale are often based on their application. To accomplish permanent results, however, the methods must be considered in relation to standards and definitions for well-defined commercial grades. If commercial grades of canned foods can be defined accurately and the grade stated on the label, laboratory methods can probably be extended far beyond their present limits. Un-

questionably considerable progress can be made; and as such methods are developed, it is believed that they will be more appropriate to the term, canned vegetables or canned foods, than the methods which are now found there. At the same time the elaboration of such methods will probably accompany or follow the adoption of standards, and progress must be slow.

In response to the secretary's request for information, several laboratories offered to collaborate, but the work undertaken was such that collaboration did not appear to be practicable. The following subjects were studied in the laboratory of the associate referee: (1) The relative composition of the juice expressed from the flesh of tomatoes and from the seed receptacles. (2) The composition of tomatoes at different stages of maturity. (3) The composition of fresh tomatoes from time to time throughout the season. (4) The influence of rainfall on the composition of tomatoes. (5) The composition of tomatoes from blighted vines. (6) The composition of canned tomatoes. (7) A study of the drained solids in canned tomatoes. (8) The composition of tomato pulp and methods for its analysis.

METHODS OF ANALYSIS.

The variation in the percentage of insoluble matter in tomatoes, especially seeds, is so great that it is believed that results expressed in terms of per cent of the entire fruit would be of little value. It was decided, therefore, to confine the analytical work to the expressed juice of cooked and raw tomatoes, both green and ripened.

As stated below, the composition of the juice of the seed receptacles is different from that expressed from the pulp. To obtain a uniform sample, the fruit was cooked before pressing out the juice. The samples under examination were cut in small pieces and placed in a flask of such size that it was not more than half full. This flask was connected with a reflux condenser and suspended in boiling water. From time to time the flask was removed from the supporting clamp and given a vigorous circulatory motion until the contents were thoroughly mixed. When the sample was thoroughly softened, the flask was removed from the boiling water bath and cooled in cold water. The contents were then pressed through a bag and filtered through paper. The analytical determinations were made on the filtered juice. Ten samples were each divided into two portions, one of which was pressed raw and the other after cooking, as described above. The results are given in Table 1. In sample No. 1228 an error may have been made in the determination of either solids or index of refraction. In samples 1237 and 1243 a more complete extraction appears to have been obtained with the cooked tomatoes than with the raw. In all other cases the results obtained by the two methods of

extraction were practically identical. On the whole, the results obtained by cooking before pressing out the juice appeared to be the more reliable.

Total solids.—The total solids were determined by drying in vacuo at 70°C. in a flat-bottom dish 3 inches in diameter. A sufficient amount of water was added to permit the uniform distribution of the solids over the entire bottom of the dish. The drying was continued until the loss between two successive weighings was negligible. Four hours' drying was found to be sufficient after the material had reached apparent dryness.

Sugar.—The sugar was determined by reduction, using Munson and Walker's method. All solutions were inverted in the cold before reduction, according to the method given in Bulletin 107. It is probable that the sugar in tomatoes is all invert sugar. This was indicated by some samples which were examined in which the determination of sugar before and after inversion gave the same results. In order to eliminate uncertainty, however, all samples were inverted.

TABLE 1.

Composition of juice pressed from raw and cooked tomatoes.

SAMPLE NO.	PER CENT SOLIDS IN VACUO		PER CENT SUGAR AS INVERT		PER CENT ACID AS CITRIC		PER CENT SUGAR IN SOLIDS		PER CENT ACID IN SOLIDS		IMMERSION REFRACTOMETER READING	
	Raw	Cooked	Raw	Cooked	Raw	Cooked	Raw	Cooked	Raw	Cooked	Raw	Cooked
1226	4.54	4.67	2.24	2.17	0.55	0.51	49.3	46.5	12.1	11.0	33.08	33.56
1228	[1]5.00	[2]4.87	2.61	2.62	0.52	0.46	52.0	53.8	10.5	9.5	33.47	33.22
1230	4.54	4.40	2.10	2.04	0.62	0.58	46.3	46.4	13.6	13.2	33.70	33.16
1232	4.60	4.73	2.04	2.28	0.57	0.53	44.3	48.2	12.4	11.3	33.21	33.63
1237	4.31	4.80	1.70	2.18	0.55	0.51	39.4	45.4	12.8	10.6	32.21	33.97
1239	4.43	4.41	2.26	2.07	0.60	0.61	51.0	46.7	13.4	13.9	32.37	32.58
1441	3.91	3.93	1.87	1.87	0.40	0.39	47.8	47.6	10.0	9.9	30.45	.....
1243	5.41	5.70	2.84	3.16	0.60	0.68	52.6	55.4	11.1	11.9	36.66	37.16
1245	4.09	4.06	1.75	1.68	0.44	0.46	42.8	41.4	10.8	11.2	31.16	31.42
1248	3.92	3.95	1.58	1.51	0.53	0.48	40.3	38.2	13.5	12.1	30.63	.....

[1] By calculation from refraction index this figure should be 4.64.
[2] By calculation from refraction index this figure should be 4.58.

Acidity.—In the case of juice pressed from fresh tomatoes, 20 grams are diluted with water and titrated with decinormal alkali, using phenolphthalein as indicator. In the examination of the canned product referred to later, it is necessary to boil to expel carbon dioxid. Because of the brownish color caused by the addition of an alkali, the sample should be diluted to at least 200 cc. The exact details employed are as follows:

Dilute 20 grams of the filtrate under examination with over 200 cc. of water. Add at least ½ cc. of phenolphthalein solution (prepared by dissolving 1 gram of phenolphthalein in 100 cc. of 95% alcohol) and titrate with sodium hydroxid until the end point is obtained. Add 1 cc. of tenth-normal hydrochloric acid, heat the solution quickly to boiling and boil one minute to expel carbon dioxid. Cool the solution quickly to about room temperature, and then add tenth-normal sodium hydroxid until the end point is obtained. The volume of hydrochloric acid added must, of course, be taken into consideration in the final result.

A number of samples of Kelly Red tomatoes at various stages of maturity were cut in two and the contents of the seed cavities carefully

separated. The juice of the two portions was expressed separately. In order that the sample might represent the various stages of maturity as exactly as possible, the entire crop on certain vines was picked at one time and several samples taken from it representing different stages of maturity of the individual tomatoes. The results are given in Table 2.

It will be noted that the composition of the juice of the seed cavities is materially different from the juice expressed from the flesh of the tomato. The per cent of sugar is much higher in the juice expressed from the flesh, while the per cent of acid is higher in the contents of the seed cavities. The significance of this in the composition of canned tomatoes and in the lack of uniformity of individual cans is discussed under "Canned tomatoes." This also explains, at least in part, why the relations pointed out between the various constituents of whole tomato pulp are not applicable to skin and core pulp.

COMPOSITION OF TOMATOES (EXPRESSED JUICE) AT DIFFERENT STAGES OF MATURITY.

Samples of tomatoes at three stages of maturity and of several different varieties were examined to determine the relative composition at different stages of maturity. To avoid lack of uniformity of rainfall and climatic conditions, the tomatoes were all gathered at the same time, and several samples taken according to the size of the individual fruits. The results are given in Table 2.

In general, the percentage of solids increases as the tomatoes become more mature, but the variation in the percentage of sugar and acid was so great that no fixed relation can be established from the analysis made. It is believed that in general the percentage of sugar increases somewhat and the percentage of acid decreases, at least during the last stages of the growth of the tomato. The variation between different samples is so great, however, that it is evident a larger number of individual fruits must be used for the determination, and a large number of analyses must be made before any conclusions can be drawn.

COMPOSITION OF FRESH TOMATOES (EXPRESSED JUICE) FROM TIME TO TIME THROUGHOUT THE SEASON.

In the summer of 1914 arrangements were made to secure samples of tomatoes from the Arlington Experimental Farm of the Bureau of Plant Industry, U. S. Department of Agriculture, and from the Maryland State Experiment Station. It was hoped that the data thus obtained would reveal the composition of tomatoes during various portions of the season, and the influence of rainfall on this composition. Through the courtesy of the officers of the two institutions mentioned, a number of

TABLE 2.

Composition of expressed juice of tomatoes of different degrees of maturity.[1]

SAMPLE NO.	DATE GATHERED AND EXAMINED	DESCRIPTION OF SAMPLE	COMPOSITION OF FILTERED JUICE			SUGAR IN SOLIDS	ACID IN SOLIDS	ACID-SUGAR RATIO	WHERE GROWN
			Solids in vacuo	Sugar as invert	Acid as citric				
			per cent	*per cent*	*per cent*	*per cent*	*per cent*		
1075	Sept. 2	Trophy, fairly ripe	5.08	1.85	0.72	36.4	15.9	2.6	Arlington Experimental Farm.
1079	Sept. 2	Trophy, one-half grown	4.39	2.17	0.66	49.4	16.9	3.3	Arlington Experimental Farm.
1080	Sept. 2	Trophy, one-quarter grown	4.47	1.56	0.71	34.9	16.0	2.2	Arlington Experimental Farm.
1076	Sept. 2	Stone, ripe	5.92	3.02	0.61	51.0	10.3	4.9	Arlington Experimental Farm.
1077	Sept. 2	Stone, one-half grown	4.53	2.19	0.60	48.3	13.3	3.6	Arlington Experimental Farm.
1078	Sept. 2	Stone, one-quarter grown	4.78	2.08	0.70	43.5	16.6	3.0	Arlington Experimental Farm.
1081	Sept. 2	Ponderosa, almost ripe	4.96	2.78	0.59	56.0	13.3	5.0	Arlington Experimental Farm.
1082	Sept. 2	Ponderosa, one-half grown	4.90	2.68	0.66	54.7	13.5	4.1	Arlington Experimental Farm.
1083	Sept. 2	Ponderosa, one-quarter grown	4.65	2.86	0.64	61.5	8.1	4.5	Arlington Experimental Farm.
1096	Sept. 7	Kelley red, full ripe, flesh	5.46	3.70	0.32	67.8	5.9	11.6	Maryland Experiment Station.
1097	Sept. 7	Kelley red, full ripe, seed cavities	5.46	3.06	0.56	56.0	10.3	5.4	Maryland Experiment Station
1098	Sept. 7	Kelley red, slightly red, flesh	5.25	3.40	0.46	64.8	8.7	7.5	Maryland Experiment Station
1099	Sept. 7	Kelley red, slightly red, seed cavities	5.21	2.67	0.81	52.1	15.6	3.3	Maryland Experiment Station.
1200	Sept. 7	Kelley red, full grown, green, flesh	5.00	2.68	0.68	53.6	13.6	4.0	Maryland Experiment Station.
1201	Sept. 7	Kelley red, full grown, green, seed cavities	4.45	1.75	1.10	39.3	24.7	1.6	Maryland Experiment Station.
1202	Sept. 7	Kelley red, one-half grown, flesh	4.73	2.47	0.56	52.3	11.9	4.4	Maryland Experiment Station.
1203	Sept. 7	Kelley red, one-half grown, seed cavities	4.50	1.98	1.01	44.0	22.4	2.0	Maryland Experiment Station.
1204	Sept. 7	Kelley red, one-quarter grown, flesh	4.42	2.62	0.28	59.4	6.2	9.5	Maryland Experiment Station.
1205	Sept. 7	Kelley red, one-quarter grown, seed cavities	4.44	2.22	0.56	50.0	12.7	4.0	Maryland Experiment Station.

[1] In this and following tables the data given were secured from juice obtained by cooking the tomatoes under a reflux condenser, thoroughly pressing through a cotton bag, and filtering through paper.

plants of several varieties of tomatoes were made available to the laboratory, and tomatoes were gathered from these plants as often as they ripened, from the time the work began until the end of the season. The results obtained from these examinations are given in Table 3.

Unfortunately, the importance of this work had not occurred to us until the season was well advanced and for that reason we did not secure data extending through the entire season. By means of the work done in 1914, both on fresh tomatoes and on canned tomatoes and tomato pulp, certain ratios were established which will be discussed later and which enabled us to repeat the work during the season of 1915 without the necessity of so many determinations. During the latter year it was decided to confine the work to one variety of tomatoes, and the Stone tomato was selected. A number of plants of this variety were made available to the laboratory by the two institutions mentioned above, and samples were taken throughout the season as often as they ripened. Unfortunately, neither season was normal, as will be seen by consulting the rainfall, which is given in Table 6.

In 1914, 4.66 inches of rain fell on the Arlington Farm in the latter half of August and only 0.70 inch during the entire month of September.

On the whole, there is an apparent diminution of solids and sugar in the several varieties of tomatoes as the season progresses. This was apparent in both seasons. This general tendency may be due in part to the fact that the rainfall was much heavier early in the season than later. The vines are known to be stronger and more resistant during the early part of the season, and it may be that the first tomatoes that ripen are better nourished and for that reason richer in solids and sugar than those ripening later after the vines have been under the strain of bearing.

The influence of rainfall is discussed in greater detail below. There is not the uniformity we had hoped to obtain between the successive gatherings of tomatoes—even of the same varieties and from the same vines. This is apparent in Tables 3 to 5, inclusive. The variations are so great that it is obvious that the results of the examination of individual samples must be disregarded and only the general tendency or the average of a number of samples considered. This variation in successive samples is doubtless due to the varying composition of the individual tomatoes, although as many tomatoes as could be secured were used in each sample. The frequency of the analyses often made it impossible to secure more than one-half dozen tomatoes in a sample.

As illustrating the variations just referred to, the following figures are pointed out, taken from Table 3, giving the percentage of solids in the juice of individual varieties of tomatoes at two successive pickings:

	Per cent solids
Kelley:	
October 1	4.24
October 5	4.60
Ponderosa:	
September 15	5.25
September 23	4.41
Jewel:	
August 31	5.62
September 4	4.72
Comet:	
August 31	5.62
September 4	4.90

INFLUENCE OF RAINFALL ON THE COMPOSITION OF TOMATOES.

It is generally believed by packers that rainfall increases the water content of tomatoes to a very material extent. It appears that tomatoes gathered immediately after a heavy rain are more sloppy on the peelers' tables, and that after canning the amount of solid meat, as determined by a screen, is less than with tomatoes gathered after a period of normal rainfall. It was desired to determine whether this condition was due to a difference in the water content of the tomatoes or to a change in the tomatoes causing them to permit the separation of the juice more readily. This subject has been discussed in part under the preceding topic. It is unfortunate that the rainfall during the seasons of 1914 and 1915 was not so distributed as to permit conclusive data on this subject. In Table 3 are given the results obtained by the examination of 7 varieties of tomatoes grown at the Arlington Experimental Farm and 3 varieties grown at the Maryland Experiment Station during the season of 1914.

Making allowance for the variation in individual samples referred to above, there is a marked tendency in most, if not all, of the varieties mentioned, for the content of solids and acid to be higher during the early part of the season than during the latter part. It is interesting to note in Table 6 that the rainfall was very much higher during the early part of the season than during the latter part. Unfortunately, this work was not begun until about September 1, 1914. The rainfall during the last half of the preceding month was 4.66 inches on the Arlington Farm, 2.66 inches of which fell on August 29. The ground was practically saturated, therefore, when our first samples were secured, and very little rain fell after that date until the end of the season. It will be noted that only 0.70 inch fell on the Arlington Experimental Farm and 0.76 inch fell at the Maryland Experiment Station during September.

During the first part of the month of October, the rainfall at the Maryland Station was no higher—up to the 12th when the last sample from that Station was secured, only 0.34 inch of rain fell. As stated under the preceding topic, we are unable to draw definite conclusions from these results regarding the influence of rainfall on the composition of the tomatoes. The general tendency to lower results as the season progresses may be due to other causes. It was hoped that during the season a heavy drenching rain might come, preceded and followed by dry or normal weather. In this we were disappointed.

TABLE 3.

Composition of expressed juice of tomatoes from time to time throughout the season.

SAMPLE NO.	DATE	DESCRIPTION OF SAMPLE	COMPOSITION OF FILTERED JUICE				SUGAR IN SOLIDS OF JUICE	ACID IN SOLIDS OF JUICE	SUGAR-ACID RATIO	WHERE GROWN
			Solids [1]	Sugar as invert	Acid as citric	Immersion refractometer at 17.5°C.				
			per cent	*per cent*	*per cent*		*per cent*	*per cent*		
1064	Aug. 31	Chalk's Early Jewell, ripe	5.62	3.08	0.59	.....	54.8	10.4	5.3	Arlington Experimental Farm.
1246	Sept. 3	Chalk's Early Jewell, ripe	3.92	1.58	0.53	30.63	40.3	13.5	3.0	Arlington Experimental Farm.
1085	Sept. 4	Chalk's Early Jewell, ripe	4.72	2.21	0.73	33.75	46.8	15.4	3.0	Arlington Experimental Farm.
1067	Aug. 31	Comet, ripe	5.62	3.00	0.51	.....	53.4	10.1	5.3	Arlington Experimental Farm.
1088	Sept. 4	Comet, ripe	4.90	2.38	0.61	34.57	48.6	12.5	3.9	Arlington Experimental Farm.
1208	Sept. 10	Comet, ripe	4.10	1.75	0.60	31.24	42.7	14.6	2.9	Arlington Experimental Farm.
1223	Sept. 15	Comet, ripe	4.09	1.78	0.59	31.48	43.5	14.5	3.0	Arlington Experimental Farm.
1068	Aug. 31	Beauty, ripe	5.68	2.61	0.46	.....	46.0	8.1	5.7	Arlington Experimental Farm.
1084	Sept. 4	Beauty, ripe	z5.32	2.80	0.64	37.25	52.6	12.0	4.4	Arlington Experimental Farm.
1213	Sept. 10	Beauty, ripe	4.12	1.77	0.59	31.70	43.0	14.2	3.0	Arlington Experimental Farm.
1220	Sept. 15	Beauty, ripe	3.95	1.66	0.56	31.11	42.0	14.1	3.0	Arlington Experimental Farm.
1215	Sept. 14	Kelley red	4.45	2.21	0.54	32.68	49.7	12.1	4.1	Maryland Experiment Station.
1228	Sept. 17	Kelley red, ripe	4.87	2.62	0.46	33.22	53.8	9.5	5.7	Maryland Experiment Station.
1233	Sept. 21	Kelley red, ripe	4.65	2.44	0.42	33.57	52.5	9.1	5.8	Maryland Experiment Station.
1234	Sept. 21	Kelley red, ripe	4.56	2.13	0.47	32.71	46.7	10.4	4.5	Maryland Experiment Station.
1252	Sept. 25	Kelley red	4.79	2.29	0.45	34.57	47.8	9.3	5.1	Maryland Experiment Station.
1255	Sept. 28	Kelley red	4.43	2.20	0.49	33.24	49.7	8.9	4.5	Maryland Experiment Station.
1260	Oct. 1	Kelley red, small	4.24	1.71	0.61	31.93	40.3	14.3	2.8	Maryland Experiment Station.
1267	Oct. 5	Kelley red	4.60	2.23	0.60	32.03	48.5	13.0	3.7	Maryland Experiment Station.
1280	Oct. 12	Kelley red	4.34	1.97	0.43	32.22	45.4	9.9	4.6	Maryland Experiment Station.
1063	Aug. 31	Livingston's Hummer, ripe	4.68	2.62	0.30	.....	56.0	6.4	8.7	Arlington Experimental Farm.
1089	Sept. 11	Livingston's Hummer, ripe	4.38	2.16	0.54	32.85	49.3	12.4	4.0	Arlington Experimental Farm.
1214	Sept. 10	Livingston's Hummer, nearly ripe	4.35	2.14	0.56	32.20	49.2	12.9	3.8	Arlington Experimental Farm.
1219	Sept. 15	Livingston's Hummer, ripe	4.21	2.06	0.49	31.41	49.0	11.6	4.2	Arlington Experimental Farm.
1240	Sept. 30	Livingston's Hummer, ripe	3.91	1.87	0.40	30.45	47.8	10.0	4.7	Arlington Experimental Farm.
1257	Sept. 30	Livingston's Hummer, small but ripe	4.23	1.78	0.45	31.83	42.1	10.6	4.0	Arlington Experimental Farm.

1206	Sept. 7	Matchless, ripe	5.04	2.86	0.52	35.19	56.7	10.3	5.5	Maryland Experiment Station.
1217	Sept. 14	Matchless, ripe	4.65	2.16	0.53	33.78	46.5	11.4	4.1	Maryland Experiment Station.
1225	Sept. 17	Matchless, ripe	4.54	2.24	0.55	33.08	49.3	12.1	4.1	Maryland Experiment Station.
1237	Sept. 21	Matchless, ripe	4.80	2.18	0.51	33.97	45.4	10.6	4.3	Maryland Experiment Station.
1253	Sept. 25	Matchless, ripe	4.07	1.66	0.44	31.77	40.8	10.7	3.8	Maryland Experiment Station.
1256	Sept. 28	Matchless, ripe	4.18	1.76	0.45	32.31	42.6	10.8	4.0	Maryland Experiment Station.
1262	Oct. 1	Matchless, ripe	4.32	1.71	0.55	32.38	39.6	12.7	3.1	Maryland Experiment Station.
1269	Oct. 5	Matchless, ripe	4.48	1.76	0.60	.....	39.3	13.5	2.9	Maryland Experiment Station.
1279	Oct. 12	Matchless, ripe	4.87	2.45	0.47	35.06	50.3	9.7	5.2	Maryland Experiment Station.
1066	Aug. 31	Ponderosa (Red), ripe	6.42	4.22	0.45	.....	65.7	7.0	9.5	Arlington Experimental Farm.
1081	Sept. 2	Ponderosa (Red), nearly ripe	4.96	2.78	0.59	.....	56.0	13.3	5.0	Arlington Experimental Farm.
1211	Sept. 10	Ponderosa (Red), nearly ripe	4.60	2.69	0.69	32.75	65.4	14.9	3.9	Arlington Experimental Farm.
1218	Sept. 15	Ponderosa (Red), ripe	5.25	3.03	0.68	35.80	57.7	12.9	4.5	Arlington Experimental Farm.
1239	Sept. 23	Ponderosa (Red), ripe	4.41	2.07	0.61	32.58	46.7	13.9	3.4	Arlington Experimental Farm.
1259	Sept. 30	Ponderosa (Red), ripe	4.47	1.98	0.59	32.84	44.3	13.4	3.3	Arlington Experimental Farm.
1065	Aug. 31	Stone, ripe	5.50	2.99	0.47	.....	54.4	8.5	6.4	Arlington Experimental Farm.
1076	Sept. 2	Stone, fairly ripe	5.92	3.02	0.61	.....	51.0	10.3	4.9	Arlington Experimental Farm.
1086	Sept. 4	Stone, ripe	5.58	2.67	0.59	36.84	47.8	10.5	4.5	Arlington Experimental Farm.
1222	Sept. 15	Stone, ripe	3.96	1.54	0.57	30.74	38.9	14.5	2.7	Arlington Experimental Farm.
1245	Sept. 23	Stone, ripe	4.06	1.68	0.46	31.42	41.4	11.2	3.7	Arlington Experimental Farm.
1207	Sept. 7	Stone, fairly ripe	4.92	2.77	0.58	34.39	56.4	11.7	4.8	Maryland Experiment Station.
1216	Sept. 14	Stone, full ripe	4.26	1.96	0.56	31.24	46.0	12.1	3.5	Maryland Experiment Station.
1230	Sept. 17	Stone, ripe	4.40	2.04	0.58	33.16	46.4	13.2	3.5	Maryland Experiment Station.
1232	Sept. 21	Stone, ripe	4.73	2.28	0.53	33.63	48.2	11.3	4.3	Maryland Experiment Station.
1251	Sept. 25	Stone, ripe	4.37	1.95	0.48	32.65	44.6	11.0	4.1	Maryland Experiment Station.
1254	Sept. 28	Stone, ripe	4.33	1.86	0.49	32.55	42.9	11.2	3.8	Maryland Experiment Station.
1261	Oct. 1	Stone, just ripe	4.42	1.80	0.60	32.63	40.8	13.6	3.0	Maryland Experiment Station.
1268	Oct. 5	Stone, fairly ripe	4.26	1.73	0.56	.....	40.7	13.2	3.1	Maryland Experiment Station.
1278	Oct. 12	Stone, ripe	4.72	2.33	0.45	33.99	49.4	9.4	5.2	Maryland Experiment Station.
1069	Aug. 31	Trophy, ripe	5.70	2.79	0.46	.....	49.0	8.1	6.0	Arlington Experimental Farm.
1075	Sept. 2	Trophy, fairly ripe	5.08	1.85	0.715	.....	36.4	15.9	2.6	Arlington Experimental Farm.
1087	Sept. 4	Trophy, ripe	4.68	2.02	0.64	33.60	43.2	13.8	3.1	Arlington Experimental Farm.
1210	Sept. 10	Trophy, ripe	4.59	1.61	0.78	32.62	35.1	17.0	2.1	Arlington Experimental Farm.
1221	Sept. 15	Trophy, ripe	4.29	1.57	0.63	32.1	36.6	14.6	2.5	Arlington Experimental Farm.

[1] Determined by drying at 70°C. in vacuo.

In 1915 the work was repeated, except that only solids and index of refraction were determined in the juice of the tomatoes and only one variety was employed. This time the work was begun with the first

TABLE 4.

Composition of expressed juice of tomatoes from time to time throughout the season (1915).

STONE VARIETY, GROWN AT ARLINGTON EXPERIMENTAL FARM[1]				STONE VARIETY, GROWN AT MARYLAND EXPERIMENT STATION			
Sample No.	Date	Per cent solids	Immersion refractometer at 17.5°C.	Sample No.	Date	Per cent solids	Immersion refractometer at 17.5°C.
2060	Aug. 6	5.32	36.05	2099	Sept. 7	5.27	36.19
2061	Aug. 10	5.66	37.25	2313	Sept. 9	5.35	36.19
2062	Aug. 13	5.31	35.70	2316	Sept. 11	4.83	33.65
2063	Aug. 17	5.14	35.44	2319	Sept. 14	5.20	35.50
2065	Aug. 18	5.49	36.76	2321	Sept. 16	5.10	35.00
2066	Aug. 20	5.13	35.51	2322	Sept. 18	4.49	32.50
2090	Aug. 23	5.04	34.86	2324	Sept. 21	4.56	33.49
2091	Aug. 25	4.62	33.49	2340	Sept. 23	4.62	33.08
2093	Aug. 27	5.17	35.15	2346	Sept. 28	5.09	35.57
2094	Aug. 30	5.15	35.47	2348	Sept. 30	4.87	34.22
2096	Sept. 1	4.84	34.65	2352	Oct. 2	4.95	34.42
2098	Sept. 3	5.19	36.02	2366	Oct. 5	4.75	33.60
2312	Sept. 8	4.96	34.52	2369	Oct. 7	5.19	35.62
2315	Sept. 10	5.14	35.85	2371	Oct. 9	4.76	33.65
2317	Sept. 13	4.19	31.15	2373	Oct. 12	4.61	33.50
2318	Sept. 13	4.57	32.75	2374	Oct. 14	5.08	33.80
2320	Sept. 15	4.32	32.20	2395	Oct. 16	4.51	32.37
2323	Sept. 20	3.94	31.05	2396	Oct. 19	4.41	32.50
2344	Sept. 27	4.28	32.22	2400	Oct. 21	4.85	34.22
				[2] 2403	Oct. 23	4.97	35.00
				[2] 2404	Oct. 26	4.23	31.80

[1] Samples were taken from ripe tomatoes.

[2] These samples being the last of the season were not entirely normal. They were badly shaped and not quite ripe. All other samples were normal and ripe.

TABLE 5.

Composition of expressed juice of tomatoes throughout the season, grown on a single vine (1915).

[Stone variety, grown at Arlington Experimental Farm.]

SAMPLE NO.	DATE	DESCRIPTION OF SAMPLE	PER CENT SOLIDS	IMMERSION REFRACTOMETER AT 17.5 °C.
2064	Aug. 18	Ripe	4.97	34.53
2067	Aug. 23	Ripe	4.77	33.60
2092	Aug. 27	Nearly ripe, sun-burned	5.13	35.07
2095	Sept. 1	1 large, 3 small	4.73	33.94
2097	Sept. 3	Ripe	4.54	32.97
2100	Sept. 8	Ripe	4.60	33.27
2314	Sept. 10	Ripe	4.88	34.82

fruit ripening from the vines set aside for the work. Unfortunately, the season was very unfavorable to tomatoes. Because of the heavy rainfall and cold weather the fruit did not begin to ripen until two or three weeks after the customary time. The results are given in Tables 4 and

5. Here again the climatic conditions are such that we are not warranted in drawing definite conclusions regarding the relation between the composition of the tomatoes and the amount of rainfall. By referring to Table 6, it will be noted that the rainfall was much heavier in the month of August than later in the season. At the Arlington Experimental Farm the tomatoes ripened first on August 6, and they continued to ripen on the same vines until September 27. In the first six days of August, just previous to the date of the first sample, 3 inches of rain fell at Arlington and the ground was thoroughly soaked.

TABLE 6.

Rainfall (in inches) at Arlington Experimental Farm and Maryland Experiment Station, 1914 and 1915.

1914				1915			
ARLINGTON EXPERIMENTAL FARM (AUG. 15–SEPT. 30)		MARYLAND EXPERIMENT STATION (SEPT. 1–OCT. 15)		ARLINGTON EXPERIMENTAL FARM (AUG. 1–SEPT. 30)		MARYLAND EXPERIMENT STATION (AUG. 15–OCT. 31)	
Day of month	Inches	Day of month	Inches	Day of month	Inches	Day of month	Inches
Aug. 22	0.06	Sept. 3	tr.	Aug. 2	0.05	Aug. 17	tr.
Aug. 25	0.40	Sept. 8	tr.	Aug. 3	0.02	Aug. 20	tr.
Aug. 26	1.00	Sept. 12	0.35	Aug. 4	2.52	Aug. 21	0.35
Aug. 27	0.01	Sept. 25	0.41	Aug. 5	0.35	Aug. 22	0.05
Aug. 28	0.40	Oct. 5	0.16	Aug. 6	0.06	Aug. 25	0.05
Aug. 29	2.66	Oct. 8	0.18	Aug. 7	0.87	Aug. 28	0.74
Aug. 30	0.13	Oct. 15	0.24	Aug. 10	0.10	Sept. 2	tr.
Sept. 12	0.26			Aug. 11	0.14	Sept. 5	tr.
Sept. 25	0.44			Aug. 12	1.47	Sept. 6	0.60
				Aug. 13	0.03	Sept. 7	0.01
				Aug. 16	0.06	Sept. 12	tr.
				Aug. 21	0.48	Sept. 19	1.11
				Aug. 23	0.08	Oct. 4	tr.
				Aug. 25	0.01	Oct. 5	0.43
				Aug. 28	0.35	Oct. 6	0.13
				Aug. 30	1.62	Oct. 7	0.21
				Sept. 6	0.63	Oct. 8	0.23
				Sept. 7	0.12	Oct. 14	0.04
				Sept. 18	0.12	Oct. 16	0.22
				Sept. 19	0.49	Oct. 20	0.42
				Sept. 21	0.36	Oct. 27	0.22

The amount of rainfall at Arlington in successive periods during the summer and the solid content of the tomato juice during the same periods are shown in the following tabular statement:

Relation of rainfall at Arlington Farm to solid content of tomato juice (1915).

DATE	RAINFALL	AVERAGE SOLIDS IN TOMATO JUICE
	inches	*per cent*
August 1–15	5.61	5.43
August 16–31	2.60	5.11
September 1–15	0.75	4.74
September 16–30	0.97	4.11
August 1–31	8.21	5.20
September 1–30	1.72	4.60

Very similar results were obtained from tomatoes grown at the Maryland Experiment Station. At this place they ripened later, the first fruit being ready to pick on September 7. During the first 7 days of this month the rainfall at the Maryland Station was 0.61 inch, and 0.74 inch fell on August 28. The ground was not as wet as at the Arlington Farm when the first tomatoes were picked at the latter place. Owing to the fact that the fruit ripened later, there was not so great a difference between the rainfall at the beginning of the season and later in the season at the Maryland Experiment Station as at the Arlington Farm. Notwithstanding this, there was a marked diminution of solids as the season progressed, though not so great as at the Arlington Farm. This suggests the probability that the diminution of solids was due, at least in part, to some other cause than variation of rainfall. The amount of rainfall and the content of solids in the juice of the tomatoes at the Maryland Station is shown in the following tabular statement:

Relation of rainfall at Maryland Station to solid content of tomato juice (1915).

DATE	RAINFALL	AVERAGE SOLIDS IN TOMATO JUICE
	inches	*per cent*
September 1–15	0.61	5.13
September 16–30	1.11	4.79
October 1–15	1.04	4.89
October 16–27	0.86	4.59
September 1–30	1.72	4.94
October 1–27	1.90	4.75

In Table 5 is given the solids content of a number of samples of tomatoes taken at successive times of ripening from a single vine grown at the Arlington Experimental Farm. These results show the same individual variation which has been pointed out in the preceding tables. Taking the figures in this table as a whole, there appears to be a tendency to a lower percentage of solids as the season progresses, although this tendency is not as marked as is shown in Table 4.

It is pointed out above that the solids content is higher in the tomatoes ripening early in the season than those ripening later in the season. As already stated, the rainfall during the last two years was also much heavier shortly before they were picked than later in the season. At the same time, as stated above, the thought suggests itself that this higher content of solids may be due to the greater strength of the vines at the beginning of the season than later. Moreover, the tomatoes ripen better during the hot weather that prevails in August than during the cooler weather in the fall. On the whole, the results do not warrant definite conclusions, and it is hoped that during the coming summer results may be obtained for a period of time which includes a drenching rain preceded and followed by dry weather.

COMPOSITION OF TOMATOES FROM BLIGHTED VINES.

The tomato crop is sometimes attacked by leaf blight (*Septoria lycopersici*). The blight usually makes its appearance before the fruit has ripened, and if climatic conditions are favorable it progresses rapidly after the ripening of the fruit begins. If rainfall occurs at about that time, it is followed by an especially rapid growth of the blight. The result is the destruction of the leaves of the plant and the imperfect development of the fruit. Fruit that is practically grown and nearly mature before the vine is destroyed by blight takes on the normal red color, and practically the flavor of ripe tomatoes. Fruit that is only partly grown takes on an external color of yellow or red, according to its state of maturity. When such fruit is cut the appearance of the section is widely different from that of ripe fruit. The color is pale pink or salmon, and the outer wall and the dividing walls between the seed receptacles are thin and pale. The composition of this blighted fruit is practically the same as that of green fruit at the same stage of maturity. Such fruit is usually rejected when offered for sale, but the dividing line between mature and immature fruit is hard to fix. The composition of the fruit on blighted vines is shown in Table 7. Each sample in this table consisted of at least six fruits. Notwithstanding this, the variations of individual samples are great, and the table is only of value because of the general tendency of the results it gives. The first three samples are of special interest. No. 1091 was nearly ripe when its development was stopped by blight. It, therefore, closely resembled normal ripe fruit in color, thickness of walls between seed receptacles, and composition of juice. Samples 1090 and 1092 were checked by blight while less mature. Their color was pale reddish yellow, the walls between the seed receptacles were thin, and the composition of the juice resembles that of green tomatoes. Samples 1093 and 1094 were different portions of the same tomatoes taken from blighted vines. They were nearly mature before their growth was checked by blight. The lower halves of the fruits were the color of normal ripe tomatoes. The upper (stem) halves were badly sunburned and probably did not color for that reason.

The remaining samples in Table 7 were taken near the end of the season—over a month after the fruit had begun to ripen in the patch. The plants were badly attacked by blight when the fruit began to ripen, but were not destroyed. The plants retained some leaves until after October 7. They bore fruit throughout the season that was normal in color and almost normal in form and appearance, though the yield was light. The fruit was separated according to size in preparing samples for analysis, as is indicated in the table. From the color of the samples and the thickness and color of the dividing walls between the sections of

TABLE 7.

Composition of tomatoes from blighted vines.

SAMPLE NO.	DATE	DESCRIPTION OF SAMPLE	COMPOSITION OF FILTERED JUICE				SUGAR IN SOLIDS	ACID IN SOLIDS	ACID-SUGAR RATIO	SOURCE
			Solids in vacuo	Sugar as invert	Acid as citric	Immersion refractometer				
			per cent	*per cent*	*per cent*		*per cent*	*per cent*		
1091	Sept. 5	Bonnie Best, below medium size, normal color, leaves practically dead	3.89	2.05	0.41	31.05	52.7	14.1	5.0	New Jersey
1090	Sept. 5	Bonnie Best, one-half grown, yellowish-red color, thin walls, leaves practically dead	3.03	1.32	0.45	26.80	43.6	14.8	2.9	New Jersey
1092	Sept. 5	Bonnie Best, one-third grown, yellowish-red color, thin walls, leaves practically dead	3.41	1.55	0.47	29.15	45.5	15.4	3.3	New Jersey
1093	Sept. 5	Bonnie Best, medium size, normal color, lower half of tomatoes	4.21	2.09	0.49	.....	49.7	11.6	4.3	New Jersey
1094	Sept. 5	Bonnie Best, medium size, sunburned, green color, upper half of No. 1093	4.56	2.15	0.43	.....	47.2	9.4	5.0	New Jersey
1548[1]	Oct. 7	Matchless, over 3 inches in diameter, normal color	4.11	1.57	0.53	31.77	38.2	12.9	3.0	Havre de Grace, Md.
1549[1]	Oct. 7	Matchless, 2 to 3 inches in diameter, normal color	4.09	1.47	0.55	31.59	36.0	13.6	2.7	Havre de Grace, Md.
1550[1]	Oct. 7	Matchless, less than 2 inches in diameter, normal color	3.97	1.47	0.49	31.20	37.0	12.2	3.0	Havre de Grace, Md.
1274	Oct. 7	Matchless, 2 to 3 inches in diameter, normal color	4.19	1.63	0.51	31.79	38.9	12.1	3.2	Havre de Grace, Md.
1275	Oct. 7	Matchless, less than 2 inches in diameter, normal color	3.63	1.35	0.48	29.39	37.2	13.2	2.8	Havre de Grace, Md.

the seed cavities, as well as the analytical results given in the table, it appears that the small tomatoes were scarcely, if at all, less mature than the large.

COMPOSITION OF CANNED TOMATOES.

As stated above, the juice expressed from the flesh of tomatoes is widely different in composition from that of the seed receptacles. The percentage of sugar is much greater in the former and the percentage of acid is greater in the latter. In peeling tomatoes for canning, the seed

TABLE 8.

Composition of juice expressed from duplicate cans of tomatoes.

[Date: October 7, 1914.]

SAMPLE		SOLIDS BY DRYING[1]	SOLIDS CALCULATED FROM REFRACTION INDEX	REFRACTION INDEX OF FILTERED JUICE (17.5°C).	VARIETY
		per cent	*per cent*		
1546	A	5.14	5.20	35.77	Great B. B.—1½ to 2 inches in diameter.
	B	5.20	5.30	36.20	
1547	A	4.05	4.08	31.18	Bonnie Best; small.
	B	3.99	4.04	31.00	
1548	A	4.11	4.22	31.77	Matchless; from blighted vine unsprayed, over 3 inches in diameter.
	B	4.44	4.63	33.46	
	C	4.40	4.63	33.46	
1549	A	4.09	4.17	31.59	Same as 1548; 2 to 3 inches in diameter.
	B	3.93	3.90	30.52	
	C	3.96	4.20	31.72	
1550	A	3.97	4.08	31.20	Same as 1548; under 2 inches in diameter.
	B	3.70	3.94	30.65	
	C	3.67	3.87	30.40	
1551	A	5.84	5.84	38.45	Large mature tomatoes.
	B	5.37	5.56	37.39	
	C	5.37	5.49	37.03	

[1] Determined by drying at 70°C. in vacuo.

receptacles are torn open more or less and the juice runs from them freely. It is probable that the juice that separates on the peeling table comes from the seed receptacles to a greater extent than from the flesh. This is especially probable if the tomatoes are not fully mature. Partly for this reason the composition of individual cans varies even in fancy hand-packed tomatoes, where the cans are filled entirely with the solid meat of the tomato without the addition of any of the juice separated on the peeling table. Moreover, the tomatoes are filled into the can as individuals, and only a small number of tomatoes are placed in a single can.

Even if the tomatoes could be placed in the can without peeling and consequent loss of juice, the contents of the individual cans would naturally vary in composition as much as the individual samples in Table 3. Where the cans are simply filled with the tomatoes without pressure, and the interstices are filled with the juice separated in the peelers' pans or pails, it is apparent that the composition of individual cans may vary considerably. This is illustrated by the data given in Table 8, in which is shown the composition of a number of duplicate cans from the same lot of tomatoes. Even these cans do not represent the average commercial pack. They represent a pack put up in the presence of representatives of the laboratory. These samples were much more uniform than the individual cans of an ordinary commercial pack. The tomatoes were pressed into the cans by hand until sufficient juice separated to fill the interstices. None of the juice separating on the peelers' tables was added to the cans. It will be noted that even under these circumstances there is sometimes a variation between duplicate cans of as much as 10% of the amount of total solids present.

STUDY OF THE DRAINED SOLIDS IN CANNED TOMATOES.

This subject was studied by the previous referee, who recommended that the investigation be continued.

From time to time for a number of years canners have attempted to define the grade of canned tomatoes ordinarily known as standard. Such attempts have been uniformly unsuccessful. A number of years ago three State canners' associations adopted a standard depending on the weight of tomatoes remaining on a sieve with a quarter-inch mesh. Unfortunately, this standard was not based on experimental work. When the attempt was made to put it into practice, it was found to be without value, and it has never been found practicable in the trade. The North Dakota Experiment Station for some years has used a modification of this method, the following details of which were given the referee by Mr. Ladd:

> We first pour the tomatoes upon a sieve, ¼-inch mesh, as prescribed by the method usually employed, and then the juice that passes through this, with the fine particles of tomato, are passed through a cheesecloth. A small square wooden frame, with sharp-pointed nails standing up at each corner, stands on the top of a good-sized beaker, the cheesecloth sagging somewhat in the center. The juice is poured on this and allowed to run as long as it flows freely, then the cheesecloth is lifted off from one end of the frame so as to pass the solution off from the clogging portions; it is then lifted from the other side of the frame back and forth, and allowed to drain as long as it freely drips without applying any pressure whatever, only the slight pressure that comes from the raising of the cheesecloth on opposite sides from time to time to move the juice forward.

The time can hardly be fixed, as tomatoes will differ; those that are overripe, or overcooked, or which have been shipped for a long distance, will not filter as rapidly as those less ripe or not cooked as much, or which have not been subjected to long-distance shipping.

It is claimed for this method that the cheesecloth retains the small particles of tomatoes which are separated in storage, shipment, or overcooking, and thus corrects, in large measure, the inaccuracy of the ordinary method.

TABLE 9.

Drained solids in canned tomatoes (laboratory pack) using screen with one-fourth inch mesh.

PROCESS	UNTREATED	FROZEN 7 DAYS AT 0°F.	SHIPPED 1,300 MILES BY FREIGHT	STORED 38 DAYS AT WINTER TEMPERATURE	STACK BURNED
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
8 minutes at 212°F. in rotating cooker.	79.7	69.4	75.2	75.9	.....
	80.1	61.8	74.0	71.9	.....
	78.1	63.7	77.7	79.2	.....
30 minutes at 212°F., not cooled..	68.0	41.7	51.1	79.1	56.5
	60.9	60.6	47.1	70.5	61.2
	59.9	53.4	41.9	71.1	.....
30 minutes at 212°F., cooled.....	73.4	59.9	62.2	75.3	.....
	74.5	59.8	60.5	77.4	.....
	73.2	54.3	72.2	74.5	.....
45 minutes at 212°F., not cooled...	70.6	54.2	54.7	72.1	63.5
	65.0	54.9	46.0	66.9	66.7
	64.7	47.9	59.2	75.7	70.4
45 minutes at 212°F., cooled.....	69.2	.....	58.9	75.7	.....
	77.1	.....	59.2	70.2	.....
	70.3	.....	59.8	72.5	.....
20 minutes at 225°F., not cooled..	74.6	61.8	69.8	73.8	60.7
	73.2	64.4	61.0	78.3	66.8
	77.0	58.1	65.2	74.8	62.7
20 minutes at 225°F., cooled.....	76.2	52.0	70.2	76.1	.....
	77.2	60.0	65.2	70.9	.....
	78.4	59.0	51.1	73.3	.....

To study this point, two sets of samples were secured and subjected to different conditions of temperature and storage, including shipment from Washington to Lawrence, Kans., and return. The samples were prepared in the laboratory, and care exercised to secure uniformity. The results are given in Tables 9 and 10.

Unfortunately the tomatoes from which these samples were prepared were so green that the canned samples were scarcely merchantable. The tomatoes were packed solid, no juice being used. After sealing, the cans

were divided into several lots which were sterilized by different methods, as shown in the tables in the column headed "Process." The various lots were then treated as stated below, and the percentage of drained solids determined by means of both a quarter-inch screen and cheesecloth as described above. These tomatoes were then treated as follows:

Frozen at 0°F.—The samples were placed in cold storage immediately after being canned and held at the temperature of 0° F. for one week.

TABLE 10.

Drained solids in canned tomatoes (laboratory pack) using both screen and cheesecloth.

PROCESS	UNTREATED	FROZEN 7 DAYS AT 0° F.	SHIPPED 1,300 MILES BY FREIGHT	STORED 38 DAYS AT WINTER TEMPERATURE	STACK BURNED
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
8 minutes at 212°F. in rotating cooker.	84.5	75.4	84.9	82.1	.....
	83.1	70.9	80.8	79.5	.....
	81.9	71.2	84.1	87.1	.....
30 minutes at 212°F., not cooled..	75.2	57.7	68.1	85.0	65.2
	69.7	67.2	58.7	78.7	68.5
	64.3	58.7	53.1	78.1	.....
30 minutes at 212°F., cooled.....	78.0	66.1	75.3	82.6	.....
	79.0	66.0	74.7	82.8	.....
	77.6	63.8	80.9	80.5	.....
45 minutes at 212°F., not cooled..	77.0	60.8	67.9	78.1	69.7
	70.8	61.1	64.8	76.0	71.5
	72.1	55.5	74.5	82.3	75.7
45 minutes at 212°F., cooled.....	76.6	.....	72.5	80.1	.....
	81.1	.....	70.3	77.3	.....
	75.7	.....	74.9	80.6	.....
20 minutes at 225°F., not cooled..	79.5	68.6	78.8	84.9	67.4
	80.7	69.6	69.4	84.2	72.6
	96.4	64.9	77.2	82.2	68.6
20 minutes at 225°F., cooled.....	81.4	61.0	79.3	82.6	.....
	82.1	69.1	78.0	78.8	.....
	82.8	63.3	59.8	78.4	.....

Stored 38 days at winter temperature.—The samples were placed out of doors for 38 days during midwinter. During this period the temperature varied from 18° to 64°. The temperature went below 28° thirteen times and below 26° ten times.

Stack burned.—The samples were placed in an oven in the laboratory and held at a temperature of from 60° to 70°C. for ten days. This was done to imitate the practice of some canneries of storing cans in a solid stack immediately after processing and without giving any opportunity for cooling.

On account of the unripe condition of the tomatoes discussed in Tables 10 and 11, it was feared the results might not be representative of a

commercial pack, and the work was repeated with a sample of tomatoes packed commercially from fully ripe tomatoes. This sample was also divided into lots which were heated for various lengths of time in addition to the processing given them at the factory. The details of the treatment given the various lots is shown in Table 11. In the selection of both samples above, all possible care was taken to obtain a uniform pack. It is to be expected that considerable variation will occur in the

TABLE 11.

Drained solids in fancy hand-picked tomatoes (commercial pack).

TREATMENT IN ADDITION TO PROCESSING AT PACKING HOUSE	SOLIDS ON ¼-INCH SCREEN	SOLIDS ON ¼-INCH SCREEN AND CHEESE-CLOTH
	per cent	*per cent*
Untreated	63.2	67.1
	60.7	66.1
	66.9	70.7
Heated in boiling water 45 minutes, not cooled	70.1	74.8
	72.2	76.6
	67.5	72.3
Heated in boiling water 45 minutes, cooled	73.9	77.5
	75.4	78.8
	74.5	78.3
Stack burned	57.1	60.9
	61.1	65.1
	59.9	64.8
Shipped 1,300 miles by express	70.5	75.0
	70.8	75.0
	71.4	75.6
Frozen 7 days at 0°F	62.2	65.7
	57.3	61.4
	51.9	56.9
Stored 38 days at winter temperature	70.3	75.2
	72.4	78.5
	71.5	76.8

individual samples examined in this manner, and it is interesting to note that this variation is much less in the determinations made with both quarter-inch screen and cheesecloth than in those made with the quarter-inch screen alone. The results shown in these tables are more uniform than can be secured with miscellaneous samples representing different lots of tomatoes, and even different localities and different portions of the season in the same locality.

It would be interesting to study the influence of the variety of tomatoes, the degree of maturity, the amount of rainfall, the locality in

which the fruit is produced, the mode of scalding, and the sizes and shape of pails and pans in which the peeled tomatoes are placed by the peelers. The figures given in the accompanying tables, of course, apply only to "solid pack" tomatoes put up with the utmost care. The variation in the amount of solid meat is, of course, much greater in tomatoes packed under commercial conditions—especially when filled by machinery.

COMPOSITION OF TOMATO PULP AND METHODS FOR ITS ANALYSIS.

Tomato pulp is now made on a very large scale for the manufacture of ketchup and soup. It is also being packed in increasing quantities in small containers for household use. If sold as tomato pulp or under any similar name without qualification, the product is supposed to consist of the fleshy portion of the tomato separated from skin, cores, and seeds, by means of a fine-mesh screen and suitably concentrated by evaporation. If manufactured from trimming stock in connection with the canning of tomatoes, that fact should, of course, be stated on the label.

During the last year a considerable number of samples of pulp of known origin, including samples manufactured in experimental runs conducted by the laboratory of the associate referee, were carefully studied. As a result of this work, it was found that in pulp manufactured from whole tomatoes a very exact relation exists between the results obtained by the following determinations in the pulp and in the filtrate obtained by throwing the pulp on a folded filter:

Total solids as determined by drying in vacuo at 70°C.
Total solids as determined by drying four hours (after apparent dryness) under atmospheric pressure at the boiling point of water.
Specific gravity of the pulp.
Specific gravity of the filtered liquor.
Index of refraction of the filtered liquor.

As a result of the data secured from this work, the following relations have been established:

S = Solids by drying at atmospheric pressure $\times$ 1.085.
$S = S' \times 1.12$.
$S = 228\ (d - 1.000) + 19.1\ (d - 1.015)$.
$S = 257.5\ (d' - 1.000)$.
$S = 0.289\ (r - 15) - 0.0185\ (r - 26.4)$.
$S = 748\ (N_D - 1.3332) - 25.5\ (N_D - 1.3376)$.
S' = Solids by drying at atmospheric pressure $\times$ 1.125.
$S' = 230\ (d' - 1.000)$.
$S' = 0.258\ (r - 15) - 0.0165\ (r - 26.4)$.
$S' = 666\ (N_D - 1.3332) - 20.7\ (N_D - 1.3376)$.

In which the symbols have the following significance:

S = Per cent solids of pulp determined by drying in vacuo at 70°C.
S′ = Per cent solids of filtrate determined by drying in vacuo at 70°C.
d = Specific gravity of pulp at 20°C.
d' = Specific gravity of filtrate at 20°C.
r = Scale reading of filtrate on immersion refractometer at 17.5°C.
N_D = Index of refraction of filtrate at 17.5°C. on Abbe refractometer.

From the specific gravity of the filtrate at 20°C., the per cent of solids of the pulp (not of the filtrate) may be ascertained from the Windisch wine table (U. S. Bur. Chem. Bul. 107, Table V, pp. 218–220). The figure 0.05 should be deducted from the percentage of solids given in that table. The solids in the filtrate may be ascertained from the index of refraction, using Wagner's table for beer and wine extract. This table is applicable without correction to the juice of fresh or canned tomatoes. When applying it to the filtrate from pulp of the usual concentration, the figure 0.17 should be deducted from the percentage of solids given. If the product has been salted, the sodium chlorid should be determined and a corresponding correction made in refractive index.

The data given above has been arranged in tabular form, but a detailed statement is not included in this report, as it has already been published.[1]

No report was made by the associate referee on cocoa and cocoa products.

REPORT ON TEA AND COFFEE.

By J. M. Bartlett (Agricultural Experiment Station, Orono, Me.), *Associate Referee.*

Work on these materials has again been confined to methods for the determination of caffein. This subject has been considered by the association for four years without much progress being made. This is partly because only a few of the members are particularly interested in the determination and but little cöoperation could be obtained, and partly because nearly every man working upon these materials has some favorite method for determining caffein, thus furnishing quite a number of methods to test out.

This year the many different methods have been studied to learn which is a practical and accurate method applicable to both tea and coffee.

The caffein of coffee is chemically the same as that of tea and, being entirely soluble in hot water, alcohol, and chloroform, can be extracted from either tea or coffee by any one of these solvents. Allen[2] uses boil-

[1] J. Ind. Eng. Chem., 1915, **7**: 602.
[2] Allen's Commercial Organic Analysis, Vol. III, Pt. II, p. 490.

ing water for both tea and coffee, and states that he has found alcohol to effect no quicker separation and it removes a larger amount of chlorophyll. Paul and Cownley[1] dried the moistened powder with magnesia and then extracted with alcohol. Hilger and Fricke[2] extracted caffein from coffee with boiling water, as did Dvorkovitsch and Stahlschmidt from tea. Sullivan in his work on coffee used boiling water, and Fuller in his method uses acidulated boiling water to extract caffein from both tea and coffee. Gorter uses chloroform and a Soxhlet extractor to extract caffein from coffee. With two exceptions the methods mentioned cause a complete extraction of crude caffein in both materials with hot water. A large volume of liquid, which must be later removed, results from filtering and washing the residues. In the method proposed this difficulty is obviated by using graduated flasks, passing the solutions through dry filters, and using aliquot portions for subsequent work. Several different methods of separating and purifying the crude caffein after extraction are used, most of which give good results when properly carried out, but some are long and tedious, and in the experience of your referee give no more accurate results than some of the shorter and less tedious methods.

Stahlschmidt's[3] method, slightly modified, has been before the association for four years, and as now presented has been changed only in minor details. The chief changes are the use of dry basic acetate of lead instead of the normal to clear the solution, and hydrogen sulphid to remove the excess of lead instead of sodium phosphate, which gives a precipitate that is very liable to run through the filter. Graduated flasks and aliquot portions are used instead of attempting to wash precipitates, which is a difficult process and incomplete with these materials. The method as recommended is as follows:

Weigh 3.125 grams of the finely powdered material, fine enough to pass through a 40-mesh sieve, into a 500 cc. flask, add 225 cc. of water, attach a reflux condenser, and boil for 3 hours. Add 2 grams of dry basic acetate of lead (Dr. Horn's) and boil 10 minutes, cool to room temperature, transfer to a graduated 250 cc. flask, make to the mark, thoroughly mix and filter through a dry filter, measure 200 cc. of the filtrate into a 250 cc. graduated flask and pass H_2S through it to remove lead. When lead is all precipitated, make the solution up to the mark and filter through dry filter. Measure 200 cc. of this filtrate, representing 2 grams of the original material, into an evaporating dish and concentrate on a steam bath to 40 cc. Wash the concentrated solution with as little water as possible into a small separatory funnel, and shake out four times with chloroform, using 25, 20, 15, and 10 cc. When extracting coffee, make the solution slightly alkaline with ammonia before extracting with chloroform. If any emulsion forms, break it up with a stirring rod and run the separate portions of chloroform

---

[1] Allen's Commercial Organic Analysis, III, Pt. II, p. 491.
[2] U. S. Bur. Chem. Bul. 107 (rev.), p. 153.
[3] Allen states that this method is applicable to the determination of caffein in coffee as well as tea (Allen's Commercial Organic Analysis, Vol. III, Pt. II, p. 491).

through a 5 cm. filter paper into a small tared Erlenmeyer flask. Remove the chloroform, dry the residue to a constant weight at 100°C. Divide weight by $\frac{2}{100}$ for percentage. If the caffein is not in pure white crystals determine the nitrogen by Kjeldahl or Gunning methods, and multiply the amount of nitrogen found by factor 3.464 for caffein.

Usually the caffein is sufficiently pure, as determined by weight, and seldom varies more than one-tenth or two-tenths per cent from the N determination. The caffein can be estimated after precipitation by iodin solution, as given in Fuller's method published in the Journal of the Association of Official Agricultural Chemists, volume 1, No. 2, page 203, omitting, however,[1] the use of animal charcoal, as that retains caffein. Or the coloring matter can be removed by dissolving the caffein in hot water, making alkaline with ammonia, and extracting with chloroform. This requires less time than purifying with iodin solution.

For the coöperative work this year a quantity of black tea and a good grade of coffee, Mocha and Java flavor, from the material used in 1914, was ground fine enough to pass a 40-mesh sieve, thoroughly mixed, and stored in tight cans. The results obtained from two laboratories besides my own are reported in the following tables:

Caffein determinations on tea and coffee.

TEA.[a]

	FULLER METHOD	STAHLSCHMIDT METHOD		STAHLSCHMIDT MODIFIED METHOD	
	per cent	*per cent*	N × 3.464 *per cent*	*per cent*	N × 3.464 *per cent*
H. H. Hanson, Maine Experiment Station, Orono, Me.	2.70	3.09	2.74	2.91	2.84
				[3]3.24	2.91
				2.97	2.94
H. C. Fuller, Industrial Institute, Washington, D. C.	2.57	2.61	.....	.....	.....
H. J. Wichmann, reported by P. B. Dunbar, Bureau of Chemistry, Washington, D. C.	.....	.....	.....	3.01	2.63
				3.05	2.53
J. O. Clarke, reported by R. E. Stallings, Atlanta, Ga.	.....	.....	.....	2.72	2.60
				2.63	2.50
J. M. Bartlett, Maine Experiment Station, Orono, Me.	.....	.....	.....	2.85	2.70
				2.85	2.74
				2.87	.....
Average	2.59	2.85	2.74	2.87	2.71

[1] Allen's Commercial Organic Analysis, Vol. III, Pt. II, p. 485.

Caffein determinations on tea and coffee—Continued

COFFEE.

	FULLER METHOD	GORTER METHOD		STAHLSCHMIDT MODIFIED METHOD	
H. H. Hanson	1.28	1.36	1.11	1.41 [1]1.60 [1]1.75	1.21 1.28 1.23
H. C. Fuller	1.12	1.06	.....	.....	.....
H. J. Wichmann	.....	.....	.....	1.40 1.41	1.17 1.12
J. O. Clarke	.....	.....	.....	1.31 1.34 1.29	1.12 1.16 1.14
J. M. Bartlett	.....	.....	.....	1.39 1.40 1.32 1.31	1.21 1.34 ..... 1.25
Average	1.20	1.21	1.11	1.36	1.20

[1] Omitted from average.

One analyst, H. J. Wichmann, has commented on the method, stating that the caffein from the tea seemed sufficiently pure to weigh directly, but that from the coffee was contaminated with some yellow material. The method as sent out was the same for coffee as for tea, but making the solution alkaline with ammonia before shaking out with chloroform gives a much whiter residue in the case of coffee.

The results obtained are very satisfactory when we consider the material, and more concordant than most results obtained in previous years by other methods, particularly when calculated from the nitrogen content. However, most of the results obtained by direct weighing are sufficiently accurate for the purpose of estimating purity of the materials from the caffein content.

So few analysts have taken part in the work and so few varieties of teas and coffees have been analyzed that your referee does not feel warranted in yet recommending the method as an official one, but considers it highly preferable to the present provisional methods given in U. S. Bureau of Chemistry Bulletin 107 (revised), which, as far as he can learn, are not being used by anyone for the determination of caffein in these products.

It is, therefore, recommended—

(1) That the Stahlschmidt method as modified in this paper be adopted as a provisional method for the determination of caffein in tea and coffee.

(2) That the method be further tried on a greater variety of teas and coffees, anticipating its adoption as an official method.

(3) That the referee for next year study methods for determining tannin in tea and coffee.

DETERMINATION OF SACCHARIN IN FOODS.

By C. B. Gnadinger (Bureau of Chemistry Food and Drug Inspection Laboratory, Chicago, Ill.)

The provisional method of the association[1] for the determination of saccharin in foods is, briefly, to macerate the solid or semisolid material with dilute alkali, centrifuge, acidify the alkaline solution, extract the saccharin with ether, evaporate the ether, and determine in the ether extract the sulphur from which the weight of saccharin is calculated. This method is not applicable to foods containing an appreciable amount of ground mustard, because the ether-soluble sulphur compounds present in mustard are extracted, in part, with the saccharin and are not separated from it by washing the ether extracts with dilute alkali. Difficulty in obtaining a clear solution for extraction, precipitation on acidifying the alkaline solution, and formation of very troublesome emulsions also render this method objectionable.

The experiments here described were made for the purpose of developing a method free from these objections. Incidentally some of the properties of saccharin were investigated.

SELECTION OF SOLVENT.

For the purpose of selecting the solvent most suitable for the extraction of saccharin, its solubility in various solvents was determined, and experiments were made to establish the number of shake-outs necessary for its extraction from aqueous and acid solutions.

The saccharin used had the following analysis:

Moisture (loss on drying over sulphuric acid)	None
Ether-insoluble matter (per cent)	0.32
Benzoic sulphinid, by Reid's method[2] (per cent)	96.20
Nitrogen present as ammonium salts	None
Total acidity calculated as saccharin (per cent)	98.03
Saccharin calculated from sulphur determined by fusion (per cent)	98.09
Melting point (°C.)	224

In determining the solubilities, a slight excess of saccharin was added to a portion of the filtered solvent in a glass-stoppered flask and allowed to stand several days at 27° to 30°C., with occasional shaking. The flask was then placed in a water bath at 25°C. for at least one hour and shaken frequently. Part of the solution at 25°C. was transferred to a weight burette by means of a pipette, closed with a piece of filter paper, and weighed from the burette into a tared dish. The solvent was evaporated spontaneously before a fan, and the residue dried to constant weight in

[1] U. S. Bur. Chem. Bul. 107 (rev.), p. 182.
[2] Allen's Commercial Organic Analysis, 4th ed., vol. 3, p. 434.

a desiccator. Similarly, the percentage of solids in the solvent was determined and a corresponding correction made. From the results thus obtained the weight of saccharin dissolved by 100 grams of solvent at 25°C. was calculated.

TABLE 1.

Solubilities of saccharin.

SOLVENT	SACCHARIN DISSOLVED BY 100 GRAMS OF SOLVENT AT 25°C.	SOLVENT	SACCHARIN DISSOLVED BY 100 GRAMS OF SOLVENT AT 25°C.
	grams		*grams*
Acetone	14.37	Chloroform	0.259
Methyl acetate	8.09	Benzol	0.129
Ethyl acetate	4.51	Toluol	0.113
Ethyl alcohol (99.5%)	3.84	Xylol	0.097
Amyl acetate	1.69	Carbon tetrachlorid	0.0067
Ether ("over sodium")	1.56	Carbon bisulphid	0.0064
Amyl alcohol	1.22	Petroleum ether, boiling point 30°–65°C.	0.0009
Water (distilled)	0.400		

Those solvents in which saccharin is much less soluble than in water need not be considered further. Of those remaining, acetone and ethyl alcohol are miscible with water, and methyl acetate is largely soluble in water. Amyl acetate and amyl alcohol have the disadvantage of high boiling points.

Ethyl acetate, ether, and chloroform were next compared as to the number of extractions necessary for the removal of saccharin from aqueous and acid solutions. The following solutions were prepared: Saccharin, 1 gram per liter and 2 grams per liter; 2 N HCl; N/5 HCl; 2 N acetic acid; N/5 acetic acid; 2 N acetic acid plus N/5 HCl. The ether and ethyl acetate used were washed three times with water and filtered; the chloroform was filtered.

One hundred cubic centimeters of solution containing 100 mg. of saccharin were pipetted into an 8 oz. separatory funnel and 50 cc. of the immiscible solvent added from a pipette. The separatory was shaken vigorously for two minutes, allowed to stand at least fifteen minutes, and the immiscible solvent drawn off into a tared dish. The extraction was repeated twice, and the three portions of solvent, in separate tared dishes, were evaporated before a fan. The dishes were then dried to constant weight in a desiccator. A blank was run, using 100 cc. of distilled water and 50 cc. of solvent, and a correction made for the solids thus found in the solvent.

The experiment was repeated, extracting 50 cc. of saccharin solution containing 100 mg. saccharin and 50 cc. 2 N HCl or 2 N acetic acid, etc., with 50 cc. of solvent. Blanks were run, using 50 cc. of distilled water instead of the saccharin solution. In some cases the extracts were ti-

trated with N/100 NaOH (phenolphthalein) as well as weighed. The agreement between gravimetric and volumetric results was excellent. All extractions were made at room temperature, 27°–30°C.

TABLE 2.

Extraction of saccharin with chloroform, ether, and ethyl acetate from aqueous and acid solutions.

IMMISCIBLE SOLVENT (50 CC. USED)	AQUEOUS SOLUTION (100 CC. EXTRACTED)		SACCHARIN EXTRACTED			TOTAL SACCHARIN EXTRACTED
	Saccharin present	Acidity	First extraction	Second extraction	Third extraction	
	mg.		*mg.*	*mg.*	*mg.*	*per cent*
Chloroform	100	0	9.5	8.7	7.6	25.8
			9.5	8.6	7.3	25.4
Do	100	Acetic, N/10	11.2	8.7	7.5	27.4
			11.2	9.2	7.7	28.1
Do	100	Acetic, N/1	16.6	13.6	10.4	40.6
			16.1	13.6	10.6	40.3
Do	100	HCl, N/10	42.5	24.8	14.0	81.3
			42.0	25.0	14.5	81.5
Do	100	HCl, N/1	50.0	24.8	12.0	86.8
			50.3	24.3	12.0	86.6
Ether	100	0	30.7	20.5	12.0	63.2
			30.8	20.0	12.0	62.8
Do	100	Acetic, N/1	39.7	23.9	13.6	77.2
			38.1	24.6	14.0	76.7
Do	100	Acetic, N/1; HCl, N/10	74.5	20.5	4.2	99.2
			74.0	19.7	5.0	98.7
Do	100	HCl, N/10	76.3	18.7	3.9	98.9
			76.5	17.7	4.8	99.0
Do	100	HCl, N/1	81.8	14.8	3.1	99.7
			82.5	14.9	2.4	99.8
Ethyl acetate	100	HCl, N/10	94.5	6.0	0.3	100.8
			94.5	6.0	0.5	101.0

Either ethyl acetate or ether may be used for the extraction of saccharin, two extractions being necessary with the former and three with the latter, when one volume of solvent is used to extract two volumes of hydrochloric-acid solution. Saccharin is more readily extracted from hydrochloric-acid solution than from acetic-acid solution. Chloroform is not a suitable solvent.

DETERMINATION OF SACCHARIN IN MUSTARD PRODUCTS.

In detecting saccharin by the method of Bianchi and di Nola,[1] the solution acidified with acetic acid is clarified with lead acetate, made acid with sulphuric acid, and extracted. This method, slightly modified, applied to prepared mustard removes very little of the interfering sulphur compounds. If, however, the solvent used for the extraction be evaporated and the residue treated with petroleum ether, most of these compounds

[1] Allen's Commercial Organic Analysis, 4 ed., vol. 3, p. 432.

are removed. The petroleum-ether extract contains a very pungent, oily, sulphur-bearing substance. By further treatment of the residue with bromin, practically all of the interfering substances are eliminated while the saccharin remains unchanged. The lead-acetate clarification yields a solution which can be readily extracted with the formation of little or no emulsion.

The following procedure is based on the method mentioned above and on the preceding solubility experiments:

METHOD FOR DETERMINATION OF SACCHARIN IN MUSTARD PRODUCTS.

Transfer 50 to 75 grams of the material (ground in a meat grinder, if necessary) to a 250 cc. volumetric flask with nearly boiling water, diluting to about 200 cc.; let stand 2 hours, shaking occasionally. Add 5 cc. glacial acetic acid, mix thoroughly and add a slight excess of 20% normal lead acetate solution. Make to mark with cold water and let stand 20 minutes. Centrifuge and pour the supernatant liquid through a folded filter. Transfer 150 cc. of filtrate to a separatory funnel, add 15 cc. concentrated HCl and extract three times with 80 cc. portions of ether, shaking the separatory for two minutes each time. Wash the combined ether extracts once with 5 cc. water and transfer the ether to a 250 cc. beaker. Add about 10 grams washed sea sand and evaporate the ether before a fan or air blast. Distribute the sand on the walls of the beaker with a stirring rod and continue the spontaneous evaporation until quite dry. Add 25 cc. petroleum ether (boiling point, 30° to 65°C.) and rub thoroughly with a "policeman." Decant through a dry 7 cm. quantitative filter paper and repeat the washing twice, using 25 cc. petroleum ether each time. Reject the petroleum ether washings and return the filter paper to the beaker containing the sand. Wash the residue on the sand with hot water and filter into a separatory funnel, collecting about 75 cc. of filtrate. Cool, add 7 to 8 cc. concentrated HCl and a distinct excess of bromin water. Let stand 5 minutes and destroy the excess of bromin with sodium nitrite solution, avoiding a large excess of the latter. Extract the acid solution three times with 50 cc. portions of ether and wash the combined ether extracts once with 5 cc. water. Evaporate the ether spontaneously and determine the sulphur in the residue by fusion with sodium peroxid or a mixture of six parts sodium carbonate and one part potassium nitrate. Conduct the fusion in a nickel crucible. Weight of $BaSO_4$ multiplied by 0.7844 gives the weight of saccharin. To the weight thus found add 0.5 mg. to correct for the saccharin dissolved by the petroleum ether. A blank should be run to determine sulphur in the fusion mixture.

The determination of sulphur in saccharin by the fusion method requires very careful manipulation to prevent loss of sulphur because of imperfect oxidation. Experiments were made to determine the possibility of converting the sulphur to sulphate by electrolyzing solutions of saccharin.

ELECTROLYTIC DETERMINATION OF SULPHUR IN SACCHARIN.

If a solution of saccharin in sodium hydroxid be electrolyzed under proper conditions, the sulphur in the saccharin will be converted quanti-

tatively into sulphate, which can then be determined as $BaSO_4$. Nitric acid or potassium hydroxid can be substituted for sodium hydroxid, but nitrates and potassium salts are occluded by the $BaSO_4$ precipitate, while sodium salts do not interfere.[1]

The results obtained by electrolyzing solutions of saccharin under different conditions are given in Table 3. The ordinary, 110-volt, direct

TABLE 3.

Determination of sulphur in saccharin by electrolysis.

NO.	MATERIAL OF ELECTRODES	AREA OF ANODE	AREA OF CATHODE	AMPERES	TIME OF ELECTROLYSIS	SOLUTION (100 cc.)	SACCHARIN	SACCHARIN RECOVERED
		sq. cm.	*sq. cm.*		*hrs.*		*mg.*	*mg.*
1	Iron	3.8	117.0	2.8–2.9	3	NaOH, N/1	100	4.7 4.7
2	Iron	117.0	3.4	2.8–2.9	3	NaOH, N/1	100	4.7 5.5
3	Nickel	1.2	117.0	2.7–2.8	3	NaOH, N/1	100	6.9 8.2
4	Nickel	117.0	1.1	2.7–2.8	3	NaOH, N/1	100	52.6 61.0
5	Platinized platinum	117.0	1.0	2.7–2.9	3	NaOH, N/1	100	8.6 12.1
6	Smooth platinum	0.9	117.0	2.8–2.9	3	NaOH, N/1	100	63.9 71.0
7	Smooth platinum	0.9	1.0	2.8–2.9	3	NaOH, N/1	100	81 9 82 0
8	Smooth platinum	125.0	92.0	2.8–2.9	3	NaOH, N/1	100	78 4 83.5
9	Smooth platinum	117.0	1.0	2.7–2.8	3	NaOH, N/1	100	86.7 89.8
10	Smooth platinum	117.0	1.0	0.7–1.0	3	Aqueous	100	8.3 9.0
11	Smooth platinum	117.0	1.0	2.4–2.6	3	NaOH, N/10	100	27.5 32.6
12	Smooth platinum	117.0	1.0	2.7–2.8	3	NaOH, N/2	100	81.6 83.9
13	Smooth platinum	117.0	1.0	2.7–2.8	3	NaOH, 2 N	100	89.4 93.7
14	Smooth platinum	117.0	1.0	0.45	3	NaOH, N/1	100	33.3 34.0
15	Smooth platinum	117.0	1.0	1.5–1.6	3	NaOH, N/1	100	56.5 57.3
16	Smooth platinum	117.0	1.0	2.7–2.9	6	NaOH, N/1	10	9.8 11.2
17	Smooth platinum	117.0	1.0	2.7–2.9	6	NaOH, N/1	50	48.1 49.0
18	Smooth platinum	117.0	1.0	2.7–2.9	6	NaOH, N/1	100	98.2 98.6
19	Smooth platinum	117.0	1.0	2.7–2.9	6	KOH, N/1	100	101.2
20	Smooth platinum	117.0	1.0	2.7–2.9	6	HNO_3, N/1	100	98.0
21	Smooth platinum	117.0	1.0	2.7–2.9	6	NaOH, N/1	[1]100	101.2
22	Smooth platinum	117.0	1.0	2.7–2.9	6	NaOH, N/1	[2]50	52.8

[1] Also 100 mg. benzoic acid.
[2] Also 100 mg. salicylic acid.

[1] Treadwell. Analytical Chemistry **2**: 368.

current was used, the strength of the current being regulated by lamps of various sizes connected in parallel; an ammeter was also placed in the circuit. Cylinders and wires were used as electrodes. Two binding posts, screwed to a wooden bar clamped on a ring stand, supported the electrodes. Experiments 1 to 9, inclusive, show the effect of using electrodes of different metals; in 6, 7, 8, and 9 the size of the electrodes was varied. Solutions containing different concentrations of NaOH were electrolyzed in experiments 9, 10, 11, 12, and 13, while in 9, 14, and 15 the strength of the current was the varying factor.

A comparison shows that smooth platinum electrodes give better results than iron, nickel, or platinized platinum electrodes. The relative size of the electrodes is not of primary importance, but it is better to use a large anode and a small cathode. The concentration of the NaOH solution should be about normal. The current strength should be 2.7 to 3.0 amperes. Accordingly, different amounts of saccharin were electrolyzed for 6 hours with a current strength of 2.7 to 2.9 amperes, using smooth platinum electrodes, the saccharin being dissolved in 100 cc. of N/1 NaOH, N/1 KOH, or N/1 HNO_3. Solution containing saccharin and benzoic acid or saccharin and salicylic acid were also electrolyzed. All reagents were tested for sulphur. Results are shown in experiments 16 to 22.

In determining saccharin in foods, dissolve the residue obtained from evaporating the ether extract in hot water and filter. Collect about 75 cc. filtrate and washings in a beaker and to this solution add 25 cc. of 16% NaOH solution. Continue the electrolysis for six hours, using smooth platinum electrodes (area of anode, approximately 120 sq. cm.; area of cathode, approximately 1 sq. cm.) and a current strength of 2.7 to 2.9 amperes. Filter the electrolyzed solution, make faintly acid with HCl, and precipitate with $BaCl_2$. Weight of $BaSO_4$ multiplied by 0.7844 gives weight of saccharin. Run a blank to determine the sulphur in 25 cc. of the 16% NaOH solution. The blank need not be electrolyzed. Results obtained on mustard products by the method described, as well as by the lead clarification method and the provisional association method, are given in Table 4. Samples A, B, and C were different brands of prepared mustard. Sulphur was determined by fusion with Na_2CO_3, and KNO_3, and by the electrolytic method.

APPLICATION OF THE LEAD ACETATE METHOD TO VARIOUS FOODS.

In applying the lead acetate clarification to foods containing no mustard the procedure described can be materially shortened as the petroleum ether extraction, bromine oxidation and second extraction with ether are unnecessary. The following method differs slightly from that of Bianchi and di Nolla previously mentioned.

TABLE 4.

Determination of saccharin in mustard.

METHOD	SACCHARIN PRESENT	SULPHUR FOUND CALCULATED AS SACCHARIN					
		Sample A		Sample B		Sample C	
		By fusion	By electrolysis	By fusion	By electrolysis	By fusion.	By electrolysis
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Provisional	none	0.035	.....	0.056	.....	.....	.....
Lead acetate clarification	none	0.015	.....	0.043	0.035	.....	.....
Do	0.100	0.135	.....	0.143	.....	.....	.....
Lead acetate clarification and treatment with petroleum ether and bromin	none	0.006	0.003	0.003	0.003	0.004	0.004
Do	none	[1]0.001	[1]0.006	.....	.....	.....	.....
Do	0.010	.....	.....	.....	.....	0.012	0.012
Do	0.050	.....	.....	0.040	0.046	.....	.....
Do	0.075	[2]0.064	[2]0.065	.....	.....	.....	.....
Do	0.100	0.082	0.086	.....	.....	.....	.....

[1] B. G. Hartmann, analyst.
[2] E. H. Berry, analyst.

METHOD FOR DETERMINING SACCHARIN IN FOODS OTHER THAN MUSTARD PRODUCTS.

Transfer 50 to 75 grams of the material, ground if necessary, to a 250 cc. volumetric flask with nearly boiling water, diluting to about 200 cc., let stand two hours, shaking occasionally. Add 5 cc. glacial acetic acid, mix thoroughly and add a slight excess of 20% normal lead acetate solution. Make to mark with cold water, mix and let stand 20 minutes. Centrifuge and pour the supernatant liquid through a folded filter. Measure a portion of the filtrate (150 cc. can usually be obtained) into a separatory funnel, add one-tenth volume concentrated HCl and extract three times with ether, using for each extraction a volume of ether equal to one-half the volume of the acid solution; shake the separatory for two minutes each time. Wash the combined ether extracts once with 5 cc. water, transfer the ether to a beaker, and

TABLE 5.

Determination of saccharin by lead clarification method.

MATERIAL	SACCHARIN PRESENT	SACCHARIN FOUND	
		By fusion	By electrolysis
	per cent	*per cent*	*per cent*
Catsup	0.200	0.198	0.196
Do	0.075	0.077	0.072
Do	0.050	[1]0.046	[1]0.048
Do	none	[1]none	.....
Canned corn	0.040	0.035	0.039
Strawberry preserves	0.030	0.032	0.034
Catawba grape juice, sulphured	0.025	[2]0.027	[2]0.026
Sauterne wine	0.010	0.010	0.010
Sweet cider	0.005	.....	0.006

[1] E. H. Berry, analyst.
[2] B. G. Hartmann, analyst.

evaporate to dryness before a fan or air blast. Determine sulphur in the residue by fusion or electrolysis. If too great an excess of lead acetate be used in clarifying, a precipitate of lead chlorid will form when the filtrate is acidified with HCl. This precipitate does not interfere and need not be removed.

In case of liquids, transfer 100 to 200 cc. to a 250 cc. volumetric flask, acidify, and clarify. Alcoholic liquids should be dealcoholized after being made alkaline with NaOH; then acidify, clarify, and extract as directed above.

Determination of saccharin in different foods by the above method are given in Table 5.

SUMMARY.

By the experiments on the solubility of saccharin, it was shown that ether and ethyl acetate are suitable solvents for the extraction of saccharin and that chloroform should not be used. The number of extractions necessary was determined, and it was found that saccharin is more readily extracted from hydrochloric-acid solution than from dilute acetic-acid solution. Continued washing of the ether extract was found to be undesirable and unnecessary. The slight solubility of saccharin in petroleum ether offers a means of separation from fat, benzoic acid, salicylic acid, etc.

The provisional association method is defective in that it is vaguely described, so that there are many sources of error which may be overlooked by the analyst. Furthermore, the method is worthless for the examination of sulphur-bearing foods such as mustard.

The determination of saccharin in the presence of mustard presents difficulties which are not met in the examination of other foods. A method for determining saccharin in mustard products was devised which gives results closely approximating the truth. Much of the detail described in this method may be omitted in the case of most foods.

The method herein described for foods containing no mustard gives very satisfactory results. The advantages over the provisional method are that the details of operation are fixed, while emulsions are avoided by clarifying with lead acetate, so that the extraction of the saccharin is easily effected.

The fusion method for determining sulphur in saccharin was found to be satisfactory. It was noted that there is danger of losing sulphur by burning off the saccharin before oxidation can take place.

An electrolytic method for determining sulphur in saccharin was developed. This method was found to be accurate and at the same time easier to operate than the fusion method.

REPORT ON PRESERVATIVES.

By A. F. Seeker (Bureau of Chemistry Food and Drug Inspection Laboratory, New York, N. Y.), *Associate Referee.*

Following the recommendations of the last report, the work this year has consisted of a trial of the Wegner procedure for the determination of formic acid as conducted by Röhrig,[1] anticipating its adoption as a confirmatory or alternative method. In collaboration with M. G. Wolf, an investigation also has been made of methods for the quantitative determination of saccharin.

FORMIC ACID.

The preliminary work reported last year by the referee indicated that fairly close agreement might be expected in determinations conducted upon the same sample by both the Fincke and the Wegner methods. It was decided therefore to submit the Wegner method to the collaborators in order to ascertain whether it would be advisable to secure its adoption as an alternative or confirmatory method.

The details of the method as submitted to the collaborators were essentially those given by Röhrig,[1] the directions for the steam distillation following the practice found most efficient in the work reported in 1913.[2]

Procedure.—Weigh 50 grams of a solid, semisolid, or heavy sirup (or measure 50 cc. in the case of a liquid) into a 300 cc. round-bottom flask, add 1 gram of tartaric acid, dilute except in the case of thin liquids, heat to boiling, distil with a current of steam until the distillate amounts to 1 liter. The mixture containing the sample should be maintained at about the same volume during the entire course of the distillation, since low results are to be expected if the volume is allowed to increase, and high results cannot be avoided if any charring or caramelization of the carbohydrates occurs. Add a few drops of phenolphthalein to the distillate and render distinctly alkaline with sodium hydroxid. Concentrate by boiling the alkaline distillate and introduce into a 100 cc. fat flask having a short neck. Evaporate the contents of the fat flask to dryness on a steam bath and place it as indicated by I in figure 1.

A is a Kipp generator containing marble fragments and hydrochloric acid for generating carbon dioxid, connected by a tube with I, the tip of which barely dips beneath the surface of the sulphuric acid when 40 cc. of the latter have been introduced into the flask. A second tube connects with II in the same way, the course of the gas then following into a third tube bent to lead into the eudiometer B—for which a Schiff's azotometer or an inverted burette may be substituted. Flask I is furnished with a small dropping funnel, the delivery tip of which is constricted in order to prevent escape of gas and to insure an even flow of acid. Both flasks I and II are furnished with thermometers reading to 250°C., the bulb of which must be immersed when the flasks contain 40 cc. of sulphuric acid. Fill the eudiometer (Schiff's azotometer or inverted burette) with caustic potash solution (1 part potas-

[1] Z. Nahr. Genussm., **19**: 4.
[2] J. Assoc. Off. Agr. Chem., **1**: 210.

sium hydroxid and 2 parts water), and place in the position shown in the diagram, within a trough or pan containing caustic potash solution. Introduce 40 cc. of concentrated sulphuric acid into flask II and a like amount into the dropping funnel of I, place flasks I and II in position, as shown in the illustration, and remove the air from the apparatus by means of a rapid current of carbon dioxid from the Kipp generator, the eudiometer being taken out of position for the first 15 minutes of this operation. Then place the eudiometer in position and continue washing with carbon dioxid until the bubbles are completely absorbed by the potassium hydroxid solution, a small flame being placed under flask II at this time until the thermometer dipping into the sulphuric acid registers 170°. Refill the eudiometer, continue the flow of carbon dioxid at ten bubbles per minute, and then slowly run the sulphuric acid from the dropping funnel into flask I, keeping the acid in flask II at 170°. Then heat the acid in flask I to 170°, maintain both it and flask II at this temperature until all the carbon monoxid has been swept into the eudiometer, the current of carbon dioxid being increased to a bubble per second for this purpose.

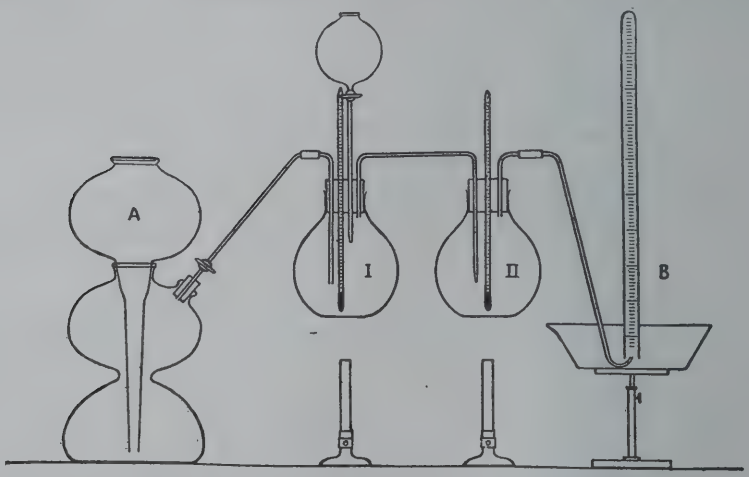


FIG. 1.—APPARATUS FOR THE DETERMINATION OF FORMIC ACID.

When the bubbles of gas passing into the eudiometer are completely absorbed, about 15 to 20 minutes after flask II reaches a temperature of 170°, discontinue the flow of carbon dioxid, place the eudiometer in a cylinder or vessel of water in which the level of the gas can be read under proper conditions and note the volume of carbon monoxid recovered. The weight of carbon monoxid can be calculated from the formula—

$$x = \frac{-v\,(b - w)\,0.0012469}{760\,(1 + at)}$$

in which—

v = volume of carbon monoxid measured over water.
b = barometric pressure.
w = tension of water vapor (or caustic potash solution).
a = 0.00367 (coefficient of expansion of gas).
t = temperature of gas in °C.

From the weight (x) of carbon monoxid obtained by this formula, calculate the weight of formic acid originally present by the formula—

$$\frac{46\,x}{28} = \text{formic acid.}$$

E. R. Lyman has combined these formulas and reduced them as follows:

$$x = \frac{vp}{t} \times 0.0007359$$

in which—

x = weight of formic acid.
v = observed volume of carbon monoxid.
p = barometric pressure in millimeters corrected for vapor tension of water at t temperature.
t = absolute temperature (273 plus observed temperature in degrees Centigrade).

Three samples were sent to thirteen collaborators to be examined by the above method. The samples consisted of (1) a standard aqueous solution of formic acid containing 0.998 gram per 100 cc.; (2) a strawberry juice containing 0.15 gram of added formic acid per 100 cc.; and (3) a fruit jam containing 0.18 per cent by weight of added formic acid. The standard formic-acid solution was prepared from Kahlbaum's formic acid, and its strength was checked both by titration and by the Fincke method of reduction of mercuric chlorid, excellent agreements being obtained by the two methods. The strawberry juice was pressed by the referee, a measured amount of the standard formic acid being added so that the content of the latter amounted to 0.15 gram per 100 cc. The fruit jam was prepared from a mixture of apple pulp, red currant pulp, and raspberry

TABLE 1.

Formic acid calculated from the amount of carbon monoxid obtained by Wegner's method, using measured amounts of a standard formic-acid solution.

ANALYST	FORMIC ACID		
	Used	Recovered	
	gram	*gram*	*per cent*
A. L. Burns, New York, N. Y....	0.0998	0.0872	[1]87.4
	0.0998	0.0936	[2]93.8
	0.0998	0.0946	[2]94.8
L. D. Elliott, New York, N. Y...	0.0998	0.0987	[2]98.9
	0.0998	0.0975	[2]97.7
E. R. Lyman, Seattle, Wash.....	0.0250	0.0206	[2]82.4
	0.1248	0.1255	[2]100.6
L. Katz, New York, N. Y.....	0.0998	0.0928	[2]93.0
W. L. Scovill, Lansing, Mich.....	0.0998	0.1092	[1]109.4
	0.0998	0.0978	[1]97.9
	0.0998	0.0956	[1]95.8
	0.0998	0.1044	[1]104.6
A. F. Seeker, New York, N. Y....	0.0998	0.0926	[2]92.8
	0.0998	0.0989	[2]99.1
	0.0998	0.0967	[2]96.9
M. G. Wolf, New York, N. Y.....	0.0998	0.0924	[2]92.6
	0.0998	0.0929	[2]93.1
	0.0998	0.0942	[2]94.4

[1] Distilled as in an ordinary determination.
[2] Introduced directly into the generator.

TABLE 2.

Formic acid recovered by Wegner's method from strawberry juice containing 0.15 gram of added formic acid per 100 cc.

ANALYST	FORMIC ACID		AMOUNT USED FOR DETERMINATION
	Found per 100 cc.	Recovered	
	gram	*per cent*	*cc.*
A. L. Burns, New York, N. Y....	0.143	95.3	50
	0.144	96.0	50
L. D. Elliott, New York, N. Y...	0.190	126.7	50
	0.166	110.7	50
E. R. Lyman, Seattle, Wash.....	0.132	88.0	50
	0.159	106.0	25
L. Katz, New York, N. Y.....	0.143	95.3	50
	0.139	92.7	50
W. L. Scovill, Lansing, Mich.....	.....	.....	.....
A. F. Seeker, New York, N. Y....	0.142	94.7	50
	0.143	95.3	50
M. G. Wolf, New York, N. Y.....	0.148	98.7	50
	0.157	104.7	50

TABLE 3.

Formic acid recovered by Wegner's method from fruit jam containing 0.18% by weight of added formic acid.

ANALYST	FORMIC ACID		AMOUNT USED FOR DETERMINATION
	Found by weight	Recovered	
	per cent	*per cent*	*grams*
A. L. Burns, New York, N. Y....	0.222	123.3	50
	0.242	134.5	32.26
L. D. Elliott, New York, N. Y...	0.188	104.5	50
	0.184	102.2	50
	0.174	99.4	[1]25
E. R. Lyman, Seattle, Wash.	0.204	113.3	50
	0.164	91.1	50
L. Katz, New York, N. Y.....	0.149	82.8	50
	0.160	88.9	50
W. L. Scovill, Lansing, Mich. ...	0.151	83.9	50
	0.188	104.7	50
A. F. Seeker, New York, N. Y...	0.199	110.5	50
	0.195	108.3	50
M. G. Wolf, New York, N. Y.....	0.190	105.6	50
	0.179	99.4	[1]25

[1] Determinations conducted by L. D. Elliott and M. G. Wolf.

pulp, made from the fruits by the referee, by heating on a steam bath with an equal weight of a mixture of commercial glucose and cane sugar. A measured amount of the standard formic acid was added to this jam, the weight of the finished mixture being so adjusted that it contained exactly 0.18 per cent by weight of formic acid. Previous to mixing with the standard formic-acid solution the jam was strained through a 15-mesh sieve to insure uniform consistency.

Results have been reported by six collaborators as shown in Tables 1, 2, and 3, determinations by the referee also being given.

The following determinations also were made by the referee upon two of the samples described above:

Strawberry juice.

	Formic acid, gram per 100 cc.
Before the addition of formic acid:	
Fincke method	0.004
Wegner method	0.008
Wegner method	0.010
After the addition of formic acid:	
Fincke method	0.149

Fruit jam.

	Per cent by weight.
Before the addition of formic acid:	
Fincke method	0.009
Wegner method	0.020
Wegner method	0.028
After the addition of formic acid:	
Fincke method	0.182

E. R. Lyman, one of the collaborators, also submits the following additional results obtained with the Wegner method:

	Formic acid, per cent by weight.
Strawberry juice prepared by analyst	0.029–0.048
Strawberry pulp prepared by analyst	0.017–0.010
Green gooseberry pulp prepared by analyst	0.010–0.015
Green gooseberry pulp prepared by analyst and containing 0.1% sodium benzoate	0.017–0 017
Tamarind paste (commercial sample)	0.030–0.033
Vinegar from mixed pickles which showed no formic acid by the Fincke method	0.007–0.057–0.040

Comparing these results with those obtained during the past two years with the Fincke method, it is evident that the latter is to be preferred for accuracy and reliability. It would appear from the results obtained by Mr. Lyman and the referee upon pure samples, and also by the reports of the collaborators, as given in Table 3, that at times some impurity passes over into the distillate which, during the decomposition of the dry residue with concentrated sulphuric acid, tends to increase the volume of gas formed beyond that due to the formic acid alone.

Comments received from collaborators were as follows:

M. G. Wolf believes that the Wegner method is too time consuming and requires too much attention.

E. R. Lyman prefers the Fincke method for accuracy and reliability.

R. W. Hilts has been unable to report upon the samples sent out by the referee owing to pressure of other work, but, having had experience in the use of both the Fincke and the Wegner methods, writes as follows: "There is no denying the fact that this method (Wegner's) is time consuming and that it requires the very close attention of the analyst during decomposition of the sodium formate. I will be interested to see what the comments of the collaborators will be. The method is not to be compared to Fincke's method for routine use. It is, however, the best confirmatory method that I know and combines a qualitative value with the quantitative determination. I believe that lactic acid is practically the

only common acid at all volatile which would yield carbon monoxid under the conditions outlined; and in view of the slight volatility of lactic acid, this objection is not very important. I believe that it would be desirable to have this method available for use as an optional method for confirmation in contested cases. If the collaborators' results are very unsatisfactory, of course this opinion might be somewhat modified."

Taking into consideration the time, attention and labor involved in the Wegner determination and also the results reported by the collaborators upon the samples sent out, it is considered inadvisable to recommend its adoption as an official method. The referee is of the opinion, however, that the method is useful for confirmatory purposes in cases when the amount of formic acid to be determined is not extremely small, due regard being paid to the apparent limits of error for the method.

It is recommended that the Fincke method adopted provisionally last year be now made official.

The referee wishes to express his acknowledgments to Messrs. A. L. Burns, L. D. Elliott, E. R. Lyman, L. Katz, W. L. Scovill, and M. G. Wolf for their assistance in this work.

SACCHARIN.

By A. F. Seeker and M. G. Wolf.

An investigation has been made of several methods that have been proposed for the determination of saccharin. These have all been found to provide for the extraction of the saccharin from solutions of the substance in which it exists by means of immiscible solvents and subsequent determinations in the residue remaining after evaporation of the solvent. This residue has been weighed directly,[1] converted into the silver salt and weighed,[2] converted into salicylic acid and determined as such,[3] or by determination of the sulphur in the residue.[4] Testoni also hydrolizes this residue by heating under pressure with 1:1 hydrochloric acid and determines the ammonia formed by distillation into standard acid.

Since all the proposed methods rely upon a complete extraction of the saccharin by shaking an aqueous solution containing it with an immiscible solvent, it was decided first to ascertain which of these is most satisfactory for the purpose in view. Ether and mixtures of ether and benzene and ether and petroleum ether have been used by various workers. Marden[5] found that chloroform is inefficient, but that ether ex-

[1] Tortelli and Piazza, Z. Nahr.-Genussm., **20**: 489; Karas, ibid., **25**: 559; Testoni, ibid., **18**: 577; Possetto and Issoglia, Giorn. farm. chim. **61**: 5.

[2] Testoni, loc. cit.

[3] Carlinfanti and Marzocchi, Boll. chim. farm., **47**: 599.

[4] Van den Diesen, Apoth. Ztg., **22**: 230; Testoni, loc. cit., U. S. Bur. Chem. Bul. 107 (rev.), p. 183.

[5] J. Ind. Eng. Chem. (1914), **6**: 315.

tracts the saccharin quantitatively with relatively small amounts of the solvent if the water layer is sufficiently acid (5 cc. concentrated hydrochloric acid to 100 cc. of solution); he also recommends amyl acetate as a solvent.

As a preliminary step, pure saccharin was prepared by acidifying a strong aqueous solution of the commercial sodium salt, washing the precipitated saccharin with water, and recrystallizing from hot water. After powdering and drying the product over sulphuric acid, it was found to yield no residue on ignition, and the sulphur, nitrogen, and ammonia (formed by acid hydrolysis) were found to agree well with the theoretical for pure saccharin.

As a result of a series of trials upon pure water solutions and upon aqueous extracts of jams containing known amounts of saccharin, it was found that ether or a mixture of ether and petroleum ether (equal parts) extract the saccharin quantitatively in three or four extractions with relatively small amounts of solvent, particularly if the aqueous layer be nearly saturated with salt. Benzene, or a mixture of benzene and ether, under the same conditions give unsatisfactory yields. In all cases when ether alone was used notable amounts of salt were retained in the solvent, and this could not be washed out without at the same time removing part of the saccharin. When aqueous extracts of food substances like fruit pulp or jam were used all the solvents retained so much impurity that the saccharin could not be weighed as such, but was estimated by fusion of the residue with sodium and potassium carbonates and determination of the sulphur as barium sulphate. Repeated washing of the saccharin solution in the volatile solvent previous to evaporation failed to remove the impurities, and the preliminary treatment of the food material with lime and alcohol-salt solution previous to extraction as proposed by Tortelli and Piazza not only failed to remove this difficulty but also yielded low recovery of the saccharin as determined by alkaline fusion of the residue.

Determinations were then made as follows: 50 grams of the material were weighed into a porcelain dish and converted into a thin paste by thorough mixing with a small amount of saturated salt solution. The mixture was then introduced into a 250 cc. volumetric flask and the dish rinsed with salt solution, the rinsings being added to the contents of the flask. About 5 cc. of milk of lime was then added and the volume made up to 250 cc. with saturated salt solution. After vigorous shaking the mixture was filtered through a dry filter and an aliquot portion of the filtrate, usually about 150 cc., introduced into a separatory funnel, acidified with hydrochloric acid, and extracted with three successive 50 cc. portions of ether. Each of the ether extracts was washed in succession with two portions of 3 cc. each of saturated salt solution, the combined

ether extracts filtered through a dry filter, and evaporated to dryness on a steam bath. The residue was then transferred to a platinum crucible by means of a little ether, again evaporated to dryness, the residue moistened with a few drops of sodium carbonate solution and fused with 3 grams of a mixture of equal parts of sodium and potassium carbonates. The melt was dissolved in water, acidified with hydrochloric acid, and the sulphur determined as barium sulphate.

Proceeding in this way, the following results were obtained:

TABLE 1.

Saccharin in food products.

SUBSTANCE	SACCHARIN		RECOVERY
	Added	Found	
	mgs.	*mgs.*	*per cent*
Orange marmalade	50	45.7	91.4
Apricot pulp	25	23.3	93.2
Rhubarb sauce	55	51.1	93.0
Do.	70	63.5	91.0

In order to duplicate as nearly as possible the type of sample represented by substances of the nature of ice-cream cones, four loaves of bread were prepared from the same flour, each approximately 1 pound in weight when baked, three loaves containing, respectively, 100, 200, and 400 mgs. of saccharin, the fourth loaf, containing no saccharin, serving as a blank. The finely powdered saccharin was intimately mixed with the flour before making the dough, and yeast alone was used as a leavening agent for the latter. The bread, after baking, was cut into large pieces and dried for a short time in a water oven. It was then ground to a moderately fine powder in a hand mill, no appreciable loss of material taking place in this process, the product obtained in this way being regarded as containing all the saccharin originally added to the flour, and its weight being used in calculating the recovery of saccharin from aliquot parts. The powder, after weighing, was preserved in tightly stoppered bottles.

The method described above was used for the extraction of the saccharin, except that it was found necessary to correct the volume of the alkaline salt solution for the space occupied by the bread, and the mixture of bread, milk of lime, and salt was allowed to stand several hours before filtering, in an attempt to secure complete solution of the saccharin.

It was found that the bread containing no saccharin gave a considerable blank in the sulphur determination upon the residue from the ether extract. This was in every case deducted from the determinations conducted upon the samples containing saccharin. The results were as follows:

TABLE 2.

Saccharin in bread.

SACCHARIN PRESENT	SACCHARIN FOUND	RECOVERY
mg. per loaf	*mg. per loaf*	*per cent*
100	62.3	62.3
200	160.9	80.5
400	264.0	66.0

As might be expected, there appears to be some difficulty in extracting the saccharin completely from the bread, and further work is in progress to secure a better method for accomplishing this.

Concerning the means for determining the saccharin in the impure residues obtained after removal of the volatile solvents used for extraction, an estimation of the sulphur seems to have found the most extended use. Direct fusion of weighed amounts of pure saccharin as in the method given above yielded results agreeing closely (98–100%) with the theoretical, and there appears to be no reason to doubt its accuracy when applied to the residues in question, provided ether-soluble sulphur compounds, like mustard oil, are absent (see pp. 25–32).

Testoni proposes to weigh the saccharin as silver saccharinate. In order to test this procedure, 0.114 gram of pure saccharin was dissolved in 10 cc. of hot water, 10 cc. of alcohol added, and the mixture cooled. After adding 10 cc. of a saturated solution of silver nitrate in alcohol, the mixture was allowed to stand overnight, filtered upon a tared Gooch, the precipitate washed with 15 cc. of absolute alcohol, dried in a water oven, cooled, and weighed. The weight of the silver salt represented 90% of the saccharin used. The experiment was repeated, employing a few drops of a saturated aqueous solution of silver nitrate as a precipitant, and adding 50 mgs. of sodium acetate to overcome the solvent effect of the free nitric acid liberated by the double decomposition between the silver nitrate and the saccharin. The silver salt in this case represented 97% of the saccharin used.

Testoni also proposes the determination of the saccharin in the impure residues by means of the ammonia formed by acid hydrolysis, distilling the hydrolized mixture for this purpose. Since the amount of ammonia formed in an actual determination is very small, this idea has been applied in modified form by weighing as ammonium chlorplatinate. The method of hydrolization has also been modified, and instead of heating under pressure as proposed by Testoni, it has been found that by boiling for three-fourths of an hour under a reflux condenser with a small amount of dilute hydrochloric acid (1 part concentrated acid and 9 parts water) complete hydrolysis takes place. After hydrolysis, the acid mixture is treated with a small amount of platinic chlorid solution (the

weight of dry platinic chlorid used to be twice the expected weight of saccharin), evaporated to dryness on a steam bath, the residue taken up in alcohol, filtered on a tared Gooch, the precipitate washed with alcohol, dried at 130°C., and weighed as ammonium chlorplatinate. Working in this way with pure saccharin the recoveries were 94, 100, and 100% in three determinations.

Accurate results have not as yet been obtained by applying either the silver salt or the ammonium chlorplatinate methods upon the impure saccharin obtained from food samples, owing to the disturbing effects of the impurities. A combination of the two has, however, been found to be fairly successful. By hydrolizing the silver salt with hydrochloric acid as described above, filtering, and converting the ammonium chlorid in the filtrate into ammonium chlorplatinate, the following results were obtained:

TABLE 3.

Saccharin in food products.

SUBSTANCE	SACCHARIN		RECOVERY
	Added	Found	
	mg.	*mg.*	*per cent*
Orange marmalade	55	57.6	104.7
Chow chow	30	30.6	102.0

It is proposed during the next year to formulate the Testoni method, or a modification of it, so that it may be used as a general method for the determination of saccharin in foods, and if possible to submit the procedure to collaborators for trial. It is hoped that the method may be so modified that the saccharin may be weighed as such previous to its determination as one of its decomposition products.

It is recommended that this work be continued.

Other references upon this subject are:

Genth. Am. J. Pharm., **81**: 536.
Bianchi and di Nola. Chem. Zentr. (1908), **2**: 2039.
Flamand. Bull. soc. chim. belg., **26**: 477.
Ledent. Ann. chim. anal., **18**: 314.
Parmeggiani. Z. oesterr. Apoth.-Ver., **46**: 179.
Condelli. Boll. chim. farm., **52**: 639.

REPORT ON HEAVY METALS IN FOODS.

By E. L. P. Treuthardt (Bureau of Chemistry, Washington, D. C.), *Associate Referee.*

Owing to the large field covered by this subject, it was found impossible to undertake all of the work recommended in the report of last year. The work was confined to testing those methods for the determination of arsenic and tin which were recommended for further study and which, it was hoped, could be recommended for adoption by the association.

In accordance with the plans of last year, the study of methods for the determination of lead in baking powder and baking-powder materials was conducted by Dr. H. E. Patten, associate referee on baking powder, and is made the subject of a separate report.

ARSENIC.

The procedure for "Method I" in the report of last year was rewritten as given below so that no references would be necessary to published directions. The 1:8 sulphuric acid strength in the generators was retained, as it is considered far more satisfactory than the stronger acid, as it is less liable to form hydrogen sulphid during reduction.

METHOD FOR THE DETERMINATION OF ARSENIC.

Adapted from method of C. R. Smith (U. S. Bur. Chem. Circ. 102). (See Sanger and Black, J. Soc. Chem. Ind., 1907, **26** : 1115).

REAGENTS.

Concentrated nitric acid and *concentrated sulphuric acid.*—Should be arsenic-free.

Dilute sulphuric acid.—1:4.

Zinc.—Arsenic-free stick zinc broken in pieces 1 inch long.

Lead acetate paper.—Heavy filter paper soaked in 20% lead acetate solution, dried and cut into pieces about 4.5 by 16 cm.

Lead acetate cotton.—Absorbent cotton soaked in 5% lead acetate solution.

Mercuric bromid paper.—Cut heavy, close-textured drafting paper (Whatman's cold-pressed if possible) into strips exactly 2.5 mm. wide and about 12 cm. long. Soak an hour in 5% solution of mercuric bromid in 95% alcohol and dry on glass rods. Cut off the ends of the strips before using.

Potassium iodid solution.—20%.

Stannous chlorid solution.—40 grams of crystals made up to 100 cc. with concentrated hydrochloric acid.

Standard arsenic solution.—Dissolve 1 gram arsenious oxid in 25 cc. of 20% sodium hydroxid, neutralize with dilute sulphuric acid, using litmus paper, add 10 cc. concentrated sulphuric acid, and dilute to 1 liter with recently boiled distilled water.

One cubic centimeter of this solution = 1 mg. As_2O_3.

Twenty cubic centimeters of this solution is diluted to 1 liter; 50 cc. of the dilute solution is made up to 1 liter; 1 cc. of this last solution = 0.001 mg. As_2O_3. This solution is used to make the standards. The dilute solutions should be made up freshly when required.

APPARATUS.

The generator bottle is a 2-ounce wide-mouth jar, connected by means of a rubber stopper to a glass tube 1 cm. by 6 cm., containing a piece of lead acetate paper rolled into a cylinder. This is connected with a similar tube loosely filled with cotton moistened with 5% lead acetate solution. The cotton should be uniformly moist in all tubes. The second tube is connected with a capillary tube 3 mm. in internal diameter and 12 cm. in length, which contains the mercuric bromid paper. All connections are made with rubber stoppers, from which white coating should be removed.

DETERMINATION.

Weigh 25 grams of sample into a porcelain casserole, add 10 cc. arsenic-free nitric acid and cover by setting a watch glass inside the rim, convex side upward. Heat until vigorous action is over, cool, and add 10[1] cc. arsenic-free sulphuric acid. Heat on a wire gauze over a flame until the mixture turns dark brown or black, then add more nitric acid in 10[1] cc. portions, heating between each addition until the liquid remains colorless or yellow, even after the evolution of SO_3 fumes. To remove completely all nitric or nitrous acids, evaporate to 5 cc.; and if on addition of water to the cooled acid nitrogen peroxid fumes are evolved, a second evaporation to white fumes is necessary.

Dilute the acid solution, transfer to a 100 cc. flask and rinse out the casserole with water. Cool and make up to 100 cc. with water. Introduce 20 cc. of this solution into a 2 oz. generator bottle, add 20 cc. 1: 4 sulphuric acid and 4 cc. potassium iodid solution. Heat to about 90°C., add three drops stannous chlorid solution and continue heating for ten minutes.

Cool the bottles in a pan containing water and ice. When cold, add about 15 grams[2] stick zinc in several pieces and connect with the tubes. Keep the bottles in ice water for fifteen minutes; take out and allow to run for one hour longer. Then remove the paper and compare with standard stains.

Run a blank test with reagents alone.

STANDARDS.

Measure out portions of the dilute standard solution containing from 0.001 to 0.050 mg. As_2O_3, and add proper quantities of water and sulphuric acid so that the generator bottle contains 40 cc. solution of 1: 8 sulphuric acid strength.

Add potassium iodid and stannous chlorid and proceed as directed under "Determination." Heating, cooling, and all other conditions should be the same for standards as for determinations.

COLLABORATIVE WORK.

Two samples were prepared for testing the methods. One was a 25% sugar solution containing 1.4 mg. As_2O_3 per kilogram and the other was a 7.5% gelatin solution containing 12.0 mg. As_2O_3 per kilogram. Results were reported from eleven collaborators as follows:

[1] Experience in this year's work has shown that 10 cc. nitric acid is frequently excessive. Portions of 3 to 4 cc. are ordinarily sufficient. See comment by Black, p. 45.

[2] This may not be enough zinc. In determination made by the referee, 30 to 40 grams were used.

Coöperative results on arsenic.

[Reported in milligrams As_2O_3 per kilogram.]

ANALYST	SAMPLE 1	SAMPLE 2
	Sugar solution containing 1.4 mg. As_2O_3 per kilogram	Gelatin solution containing 12.0 mg. As_2O_3 per kilogram
C. L. Black	1.9	14.3
	1.7	13.3
V. B. Bonney	1.3	9.0
		9.8
L. D. Ellicott	.....	10.0
	1.8	12.0
	2.0	16.0
	1.6	15.0
	.....	*20.0
L. Feldstein	0.8	10.2
	0.8	10.1
S. Ginsburg	*4.0	*20.0
L. F. Hoyt	*2.2	12.8
L. A. Salinger	*0.6	*5.8
C. C. Steere	1.0	*5.0
G. W. Trainor	*0.4	*6.0
	*0.2	*5.0
E. L. P. Treuthardt	1.8	10.0
	1.8	12.0
	1.4	12.8
	1.4	13.2
H. A. Whitman	*0.3	*2.5
Average	1.4	11.1
Average excluding results marked (*)	1.5	12.0
Results excluding those marked (*) range from	0.8 to 1.8	9.0 to 16.0

L. D. Elliott also determined arsenic in the samples by the following method:

Heat the sample for an hour with dilute hydrochloric acid, oxidize with bromin water, make alkaline with ammonia, and add magnesia mixture and disodium hydrogen phosphate to bring down the arsenic. Filter and wash the precipitate, dissolve it in 1:3 hydrochloric acid, proceed with the reduction, and follow the method as sent out, substituting 1:3 hydrochloric acid for 1:8 sulphuric acid.

Results obtained, in milligrams per kilogram.

Sample 1..... 2.5, 2.4, 2.4, 2.5
Sample 2..... 18.0, 18.0, 18.5, 17.5

COMMENTS BY COLLABORATORS.

C. L. Black: In order to have the arsenic color strips of the determinations and standards comparable it is necessary to take all possible precautions to get them of the same intensity. The rate of evolution of the gas is the main factor affecting the intensity, so that I prefer to cool the solutions to a *definite temperature*. Even then I often find that standards give off the gas at a much faster rate, thereby producing longer, light-colored strips. Less than 10 cc. of nitric acid (e. g., 3 to 4 cc.) can be introduced at a time in the digestion, as it is the number of additions

rather than the amount which affects the digestion. I attempt to use such dilution that the final reading be 0.010 to 0.020 mg., the limits of greatest accuracy.

L. D. Elliott: I do not think 1:8 sulphuric acid is at all reliable. My readings showed wide variations, although run under identical conditions.

S. Ginsburg: I * * * found the length of the stains to vary considerably for equal aliquots, and even the standards behaved almost as erratically. Hydrochloric acid is invariably employed for arsenic work in the New York laboratory and check results are readily obtainable.

L. A. Salinger: The wet cotton used was pressed out, then shredded with the fingers, and placed very lightly and evenly in the tubes. This could be used a second or third time. The solutions were cooled in a bath to 15°C. before adding zinc and were then kept there fifteen minutes before removing. Temperature makes quite a difference in the stains.

C. C. Steere: The specified time for evolution of arsin appears to be too short. Arsin in some cases was evolved for more than one-half hour after the time limit was reached. With the dilute acid solution, temperature conditions seem to be more important than with more concentrated acid. Scarcely any hydrogen was evolved with bottles in ice water in case of the standards. Perhaps the sensitized bands could be rendered more sensitive by the addition of some catalytic substance to the mercuric bromid. The more sensitive band would lessen the weight of the speed of evolution factor.

H. A. Whitman: The chief difficulty appears to be in securing uniformity in the rate of evolution of the gas in all cases, since variations in the rate give corresponding changes in the character of the stains as to length, depth of color, etc. To secure the best results the solution should be perfectly clear and colorless, the strength of acid should be the same in all cases, and the kind and weight of zinc used and the amount of surface of zinc exposed to the action of acid should be as nearly the same as possible. Fresh pieces of zinc give a slower rate of evolution than pieces which have been previously used, washed, and used again. One piece of stick zinc 1 inch long weighed almost exactly 15 grams. (See footnote on page 44.)

DISCUSSION OF RESULTS.

Two results on sample 1 are correct, 9 are high, and 8 are low. About half of the results (9 out of 19) are between 1.0 and 1.8, while about two-thirds (13 out of 19) are between 0.8 and 2.0. On sample 2, 2 results are correct, 9 are high, and 11 are low. About half of the results (10 out of 22) are between 10.0 and 14.0 and about two-thirds (15 out of 22) are between 9.0 and 16.0. The results deviate either way from the correct values, so that the errors of the averages are small. For sample 1 it is practically 0. About one-third of the results have an abnormally great deviation, and these mainly show loss of arsenic. By excluding these results the averages are raised; the average thus obtained for sample 2 is the correct value.

In view of the small amounts of arsenic present, many of the results are fairly satisfactory, although there is great discrepancy among some. There still appears necessity for more careful regulation of the conditions of operation.

The chief trouble noted by the collaborators was in regulating the evolution of arsin so that uniform stains would be obtained in standards and determinations. It is suggested that further study be made of the factors affecting the evolution, namely, concentration of solution, strength of acid, temperature, amount of zinc surface, condition of zinc, as well as time to be allowed for evolution. It does not seem advisable, however, to spend too much time on the minor details before adopting a method of this sort, as each analyst will by practice attain a uniformity in procedure which enables him to get consistent results. The procedure should be improved, however, so as to reduce the personal equation to a minimum.

Where loss of arsenic occurs it would be well to investigate to see whether the loss occurs during digestion or is due to insufficient evolution of arsin.

It is believed that further study of this method should also be made relative to its application to specific substances such as gelatin, where it is not necessary to destroy the organic matter with nitric and sulphuric acids (note the method used by L. D. Elliott). Frequently in methods of this sort, as pointed out by C. L. Black, there is greater discrepancy between standards and determinations, which may be corrected by the addition of organic matter to the former.

As recommended last year, the Marsh procedure should be made the subject of study so that it may be applied to the determination of arsenic in the amounts in which it is present in food products.

TIN.

The gravimetric and volumetric methods for tin recommended last year for further study were revised, but not essentially altered.

DIGESTION OF SAMPLE.

Weigh 100 grams of sample into an 800 cc. Kjeldahl flask and add 100 cc. concentrated nitric acid. Allow to stand overnight, or else place flask on a wire gauze over a free flame and heat until the contents boil quietly. Add 50 cc. of concentrated sulphuric acid and heat until white fumes are generated, then add 10 cc. concentrated nitric acid and continue heating as before. Repeat the addition of nitric acid until the solution remains clear after boiling off the nitric acid fumes.

GRAVIMETRIC METHOD.

Add 200 cc. of water to the digested solution and pour into a 600 cc. beaker. Rinse out the Kjeldahl flask with three portions of boiling water so that the total volume of the solution is about 400 cc. Allow to cool, add concentrated ammonia until just alkaline, and then make about 2% acid with hydrochloric or sulphuric acid. Place the covered beakers on an electric hot plate at about 95° temperature and pass in a slow stream of hydrogen sulphid for an hour. Digest on the hot plate for an hour and allow to stand overnight.

Filter the tin sulphid on an 11 cm. filter. Wash with three portions of wash solution alternated with three portions of hot water. The wash solution is made up of 100 cc. of saturated ammonium acetate, 50 cc. of glacial acetic acid, and 850 cc. of water. The filter papers used in this method are C. S. & S., No. 590, white ribbon.

Place the filter and precipitate in a 50 cc. beaker and digest with three successive portions of ammonium polysulphid, bringing to a boil each time and filtering through a 9 cm. filter. Wash with hot water. Acidify the filtrate with acetic acid, digest on the hot plate for an hour, stand overnight, and filter through a double 11 cm. filter. Wash with two portions of wash solution alternated with hot water and dry thoroughly in a weighed porcelain crucible. Thorough drying is essential to the success of the determination. Ignite very gently at first and later at full heat of Bunsen flame. Finally heat strongly with large burner, or Meker burner, having the crucible partly covered. Stannic sulphid must be gently roasted to the oxid, but the oxid may be heated strongly without loss due to volatilization.

Weigh the stannic oxid and calculate to metallic tin, using the factor 0.7881.

VOLUMETRIC METHOD (BAKER).

After digestion of material, precipitate the tin in the usual way by hydrogen sulphid. Filter the precipitate upon asbestos in a Gooch crucible with a false bottom, using suction. Wash the precipitate a few times and then push the false bottom, asbestos pad, and tin precipitate into a 300 cc. Erlenmeyer flask. Remove all traces of precipitate from the inside of the crucible by means of a jet of hot water and a policeman. Use a minimum amount of water for washing.

Add 100 cc. of concentrated hydrochloric acid and 0.5 gram of potassium chlorate to the flask. Boil for 15 minutes, making about four more additions of smaller amounts of potassium chlorate as chlorin is boiled out of the solution. The chlorate is best added with a small glass spoon. Wash the particles of potassium chlorate from the neck of the flask with water and give a final boiling to remove chlorin. Finally add about 1 gram of aluminum foil, free from tin, to dispel the last traces of chlorin.

The flasks, in duplicate, are attached, as described below, to a large Kipp generator charged with pure marble and hydrochloric acid. The carbon dioxid passes through a scrubber containing water and is then divided into two streams by means of a Y tube, each stream of carbon dioxid entering one of the flasks by means of a long rubber tube connected with a bulbed tube passing through the rubber stopper of the flask and having its lower end near the surface of the liquid in the flask. The carbon dioxid leaves the flask by a second bulbed tube, the opening of which is near the top of the flask. This glass tube is connected by a long rubber tube to a second glass tube about 10 inches long which is immersed in a cylinder containing water. This gives a water seal to the delivery tube and a pressure which the Kipp apparatus must overcome. It also obviates any violent flow of gas when not desired and permits a gas pressure in the Erlenmeyer flask. Pure seamless black rubber tubing and $\frac{3}{8}$-inch glass tubing are used to form the connections specified.

After the flasks are connected, raise the tubes in the water seal cylinders so that the Kipp apparatus has practically no pressure to overcome. Allow carbon dioxid to run through for a few minutes.

Drop the tubes to the bottom of the cylinders, creating pressure in the flasks. Lift the rubber stoppers of the flasks alternately about a dozen times, in order to pump out any air remaining in the flasks.

Slightly raise the stopper on one of the flasks and quickly drop about 2 grams of aluminum foil into the flask. The foil should be folded into a strip about 1 cm.

wide and slightly bent so as to prevent it from striking directly on the bottom of the flask. After the aluminum has entirely dissolved, raise the tubes in the cylinder to allow carbon dioxid to pass through, place the flasks upon electric hot plates, and heat to boiling.

After boiling for a few minutes, remove the flasks from the hot plates and cool in ice water, while still under carbon dioxid insulation. Lower the tubes in the cylinder. When cool, disconnect the flasks one at a time, putting a glass plug into the carbon dioxid inflow. Wash the tubes, rubber stopper, and sides of the flask with air-free wash solution, add starch paste, and titrate at once with N/100 iodin.

If it is desired to titrate by an excess of N/100 iodin the iodin is run into the flask while it is still connected with the carbon dioxid stream. The tubes are then washed out and the excess of iodin titrated with sodium thiosulphate.

The rubber connections should be washed with water after each determination.

REAGENTS.

Air-free wash solutions.—Dissolve 20 grams of sodium bicarbonate in 2 liters of boiled distilled water and add 40 cc. of concentrated hydrochloric acid. Make up fresh each day.

N/100 iodin.—1.27 grams of iodin and 2 grams of potassium iodid diluted to 1 liter with water. This should be standardized daily against tin solution, containing asbestos, following the above procedure, omitting the precipitation and boiling with hydrochloric acid and potassium chlorate.

N/100 sodium thiosulphate.—2.48 grams $Na_2S_2O_3$ made up to 1 liter with water.

Standard tin solution.—Dissolve 1 gram of tin in about 500 cc. of concentrated hydrochloric acid; make up to 1 liter with water; 1 cc. = 1 mg. of tin.

COLLABORATIVE WORK.

Two samples were analyzed by fourteen collaborators. The first sample was a 35% sugar solution containing 23.4 mg. of tin per 50-gram portion, and the second was made up of equal parts water and dealcoholized wine and contained 14.3 mg. of tin per 50-gram portion.

Coöperative results on tin.

[Reported in milligrams tin per 50-gram sample.]

ANALYST	SAMPLE 1		SAMPLE 2	
	Sugar solution containing 23.4 mg. tin per 50 grams		Wine solution containing 14.3 mg. tin per 50 grams	
	Gravimetric	Volumetric	Gravimetric	Volumetric
C. L. Black	23.5	.....	15.2	.....
	23.9	.....	14.6	.....
L. B. Burnett	21.6	21.4	12.5	12.6
	.....	21.8	.....	12.5
R. W. Clough	.....	23.4	.....	14.6
	.....	21.5	.....	14.6
L. D. Elliott	23.4	21.3	10.3	12.1
	24.4	[1]23.1	10.6	[1]10.3
W. J. Foley	.....	23.0	.....	14.0
	.....	22.9	.....	13.9
	.....	23.3	.....	13.9

[1] Reduced with antimony instead of tin.

Coöperative results on tin—Continued.

ANALYST	SAMPLE 1		SAMPLE 2	
	Sugar solution containing 23.4 mg. tin per 50 grams		Wine solution containing 14.3 mg. tin per 50 grams	
	Gravimetric	Volumetric	Gravimetric	Volumetric
S. Ginsburg	24.4	.....	15.1	.....
	24.4	.....	15.3	.....
L. F. Hoyt	24.8	22.7	15.5	13.1
	24.3	.....	13.1	13.3
	.....	22.4	.....	13.2
H. M. Miller	.....	22.7	.....	13.5
	.....	22.7	.....	.....
	.....	22.7	.....	.....
	22.2	22.7	12.3	9.5
	22.1	22.4	12.5	12.3
F. J. Montgomery	24.0	22.3	.....	12.9
	26.0	.....	.....	.....
	20.1	.....	.....	.....
W. B. D. Penniman	19.8	[2]20.1	15.0	[2]15.0
H. R. Smith	.....	22.6	.....	11.9
	.....	22.4	.....	11.6
G. W. Trainor	22.6	20.9	13.6	14.1
	20.6	20.8	13.8	
E. L. P. Treuthardt	23.2	22.9	14.2	14.2
	21.4	22.7	14.1	14.1
H. A. Whitman	22.7	20.2	12.7	12.0
Highest	26.0	23.4	15.5	15.0
Lowest	19.8	20.1	10.3	9.5
Average	23.0	22.2	13.6	13.0

[2] Tritrated with N/20 iodate solution.

Two of the collaborators considered their results by the gravimetric method too unsatisfactory to report. One collaborator was unable to report results by the volumetric method for the same reason.

COMMENTS BY COLLABORATORS.

L. D. Elliott: The reduction of the tin in the volumetric method requires practice in manipulation before reliable results can be obtained. In my duplicate of each sample I reduced the solution with antimony and connected the flask, after boiling the contents two minutes, by means of a tube to a solution of sodium bicarbonate.

H. A. Whitman: Sulphid precipitation was made in a solution containing about 5 cc. concentrated hydrochloric acid for every 100 cc. of solution, which is about 2% acidity in true HCl. In the gravimetric method stannic oxid was treated with two drops of nitric acid, reignited, dried, and weighed. In the volumetric method the aluminium foil added to dispel chlorin should be added gradually in small pieces if the solution is hot, but it may all be added at once if the solution is first cooled. Excess of iodin was added in the titration and run back with thiosulphate. The end point with starch was not very sharp and inclined to be fugitive, somewhat more so with the samples than with standards, leading probably to low results. Both methods are rather long and tedious and are not ideal for general use. Would not consider it fitting to report results closer than thousandths of a per cent.

DISCUSSION OF RESULTS.

Considering the gravimetric method, the results on sample 1 show one to be correct, nine to be high, and ten to be low. On sample 2, six results are high and eleven are low. The two lowest results on each sample have a deviation greater than −2.0. Excluding these results in obtaining the averages would give averages of 23.3 and 14.0, respectively.

The results obtained by the volumetric are slightly lower than by the gravimetric. One correct result was reported on sample 1, and the rest were all low. Two of the results had a deviation greater than − 2.8 and four had a deviation greater than − 2.0. On sample 2, three results were high and twenty were low. Four results had a deviation greater than − 2.3 and six had a deviation greater than − 2.0. By excluding these very low results, new averages could be obtained which would naturally be closer to the amounts present in the samples.

There appears a tendency to get lower results by the volumetric method, but when the details of this procedure are observed it is quite possible to get satisfactory results. On the whole, the results on the determination of tin have been highly satisfactory. Both of the above methods have been tested by the association for three years. Much work has been done on both in the Bureau of Chemistry and in commercial institutions especially interested. From the experience of the referee, in connection with the work of the association and in other directions, it is felt that the association would be justified in adopting the two methods. The gravimetric determination is rather tedious, but is suitable where only occasional determinations are to be made. For the examination of a large number of samples the convenience of the volumetric method is very apparent.

It should be noted that the method of acid digestion and precipitation by hydrogen sulphid is applicable to the determination of metals other than tin. Further work on tin should be in the investigation of methods applicable especially to that metal, notably, electrolytic methods and the method of Alexander, Bloomberg, and Lourie (J. Assoc. Off. Agr. Chem., 1915, **1**: 259 (5)), which was tried to a slight extent last year.

Concluding the report on heavy metals, attention is called to the fact that this work requires careful, neat, and accurate manipulation. This is especially evident in the lengthy procedures for the determination of tin. This work should be undertaken by experienced analysts who are willing to devote considerable time in preliminary experimentation and who pay close attention to details. It is not easy to determine minute amounts of metals in a large excess of organic matter, and simplicity of method should not be set above accuracy. Reliance should not be placed upon close checking of duplicates, but methods should be judged by

ability to get correct results when substances of known composition are examined.

Finally, attention should be called to the fact that the term "heavy metals" does not seem to apply to a subject which will soon include aluminum, nickel, copper, and zinc.

RECOMMENDATIONS.

It is recommended—

(1) That coöperation with the associate referee on baking powder in the study of methods for the determination of lead in baking powder and baking-powder materials be continued.

(2) That the gravimetric and volumetric methods for tin, tested this year, be adopted by the association as provisional.

(3) That further study be made of other methods for the determination of tin.

(4) That further study be made of the Gutzeit determination for arsenic tested this year, especially as to conditions affecting the evolution of arsin. If possible, a procedure should be devised which may be adopted as provisional.

(5) That study be made of the various modifications of the Gutzeit method for arsenic as applied to specific substances such as gelatin, following the procedures described in U. S. Bureau of Chemistry Circular 102.

(6) That a study of some modification of the Marsh method for the determination of arsenic be made.

(7) That the methods for the determination of copper, zinc, nickel, and aluminum in food products be made the subject of study by the association as soon as possible.

(8) That the designation of this portion of the work be changed to "Metals in Foods."

Adjourned at 5.05 p.m. for the day.

SECOND DAY.

TUESDAY—MORNING SESSION.

REPORT ON THE SEPARATION OF NITROGENOUS BODIES. (MILK AND CHEESE.)

By A. W. Bosworth (Agricultural Experiment Station, Geneva, N. Y.), *Referee.*[1]

The work of your referee has been confined to a study of the proteins of goat's milk and the results of this investigation will appear later as a bulletin from the New York Agricultural Experiment Station.

In order that a complete study of the separation of the nitrogenous bodies in milk be made it is necessary that we fully understand the chemical properties of each of the substances present. This is quite evident if we consider the possible production of nitrogenous bodies from casein and albumin by the action of the reagents used to remove them as a preliminary step in the study of the other nitrogenous bodies in milk.

Your referee would therefore recommend that a thorough study of the chemical properties of the albumin of milk be made by the next referee.

The President announced the appointment of the following committees:

Committee on nominations.—W. B. Ellett, Blacksburg, Va.; J. M. Bartlett, Orono, Me.; T. C. Trescot, Washington, D. C.

Committee on resolutions.—R. J. Davidson, Blacksburg, Va.; C. S. Brinton, Philadelphia, Pa.; A. S. Mitchell, Washington, D. C.

Committee on auditing.—C. S. Cathcart, New Brunswick, N. J.; J. K. Haywood, Washington, D. C.; W. L. Dubois, Hershey, Pa.

Dr. Harvey W. Wiley and C. S. Hudson were appointed to represent the association at the second Pan-American Scientific Congress, held in Washington December 27, 1915, to January 8, 1916.

[1] Presented by P. F. Trowbridge.

REPORT OF SECRETARY-TREASURER FOR THE YEAR 1914-15.

By C. L. ALSBERG (Bureau of Chemistry, Washington, D. C.),
Secretary-Treasurer.

1914	RECEIPTS.	
Nov. 16.	Balance on hand	$161.43
Nov. 18.	1913–14 dues from 3 States (Alabama, Massachusetts, and Vermont)	6.00
	Dues for the year 1914–15 from 69 Federal, State, and municipal organizations and 2 honorary members	142.00
	Total	$309.43

1914	DISBURSEMENTS.	
Nov. 18.	Telephone calls, Raleigh Hotel	$1.20
	Tips, Raleigh Hotel	4.00
Dec. 7.	1,000 special request envelopes	22.00
Dec. 19.	Postage	2.00
1915		
Jan. 14.	6 circulars, Superintendent of Documents	0.30
Feb. 2.	2 bulletins, Superintendent of Documents	0.50
Feb. 8.	Postage	2.00
Feb. 10.	Printing 700 circulars	9.75
June 3.	Post office box rent and key	0.53
June 19.	Printing 1,000 letterheads	3.75
July 2.	Post office box rent	1.00
Aug. 30.	Postage, sending out announcements of meeting	5.00
Aug. 31.	Envelopes, sending out announcements of meeting	0.75
Sept. 3.	Printing announcements of meeting	19.75
Sept. 20.	Post office box rent	1.00
Oct. 21.	Printing 1,000 letterheads	4.50
Nov. 2.	6 sheets bristol paper	0.36
Nov. 4.	350 badges	28.00
	1,000 special request envelopes	22.00
	Bank balance	181.04
	Total	$309.43

FINANCIAL STATEMENT OF THE JOURNAL OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

	RECEIPTS.	
5 cash subscriptions at $4 each		$20.00
Checks received		2,131.40
Check from secretary-treasurer for Irving C. Bull's subscription		4.00
Total receipts		$2,155.40
Interest credited (Sept. 30, 1915)		6.33
		$2,161.73

1915	DISBURSEMENTS.	
June 3.	1,000 special request envelopes	$22.00
June 10.	Postage	10.00
June 11.	Postage	5.00
June 12.	Refund on subscription	1.00
June 19.	Refund on subscription	1.00
June 25.	1,000 special request envelopes	22.00
June 26.	2 refunds on subscriptions at $1 each	2.00

REPORT OF SECRETARY-TREASURER FOR THE YEAR
1914–15—*Continued.*

June 29.	Agent's commission on subscription	$0.50
	Secretary-treasurer, checks deposited	3.00
June 30.	Stamps (cash)	3.00
July 7.	Mimeographing 2,000 letters	5.50
July 8.	Stamps (cash)	1.00
July 20.	Stamps (cash)	1.00
July 26.	100 postal cards (cash)	1.00
July 30.	Refund on subscription	1.00
Sept. 8.	Williams & Wilkins Co., on account	1,500.00
Sept. 22.	Stamps (cash)	1.00
Oct. 5.	3 refunds on subscriptions at $1 each	3.00
Oct. 6.	Stamps (cash)	0.25
Oct. 15.	Refund on subscription	1.00
Oct. 18.	Refund on subscription	1.00
Oct. 26.	Refund on subscription	1.00
Oct. 30.	2 refunds on subscriptions at $1 each	2.00
Nov. 1.	Postage (each)	1.00
	Bank balance	569.48
	Cash on hand	3.00
		$2,161.73

REPORT ON JOURNAL OF ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

By C. L. Alsberg (Bureau of Chemistry, Washington, D. C.), *Chairman, Board of Editors.*

The president of the association will recall that last year the association instructed the executive committee to undertake the establishment of an official journal of the association, which was to be a quarterly, and which was to contain the proceedings, papers that are presented before the association, and matters of scientific interest to food and drug—particularly food control—officials, and also the official methods.

Now, following those instructions, the executive committee canvassed the various publishers who seemed to be possibilities, and finally decided to make an agreement with Williams & Wilkins Co., of Baltimore. There were a number of reasons for making that selection, aside from the question of the favorable terms of the contract which the Williams & Wilkins Co. was ready to give to the association, and those others reasons were that the Williams & Wilkins Co. has had a great deal of experience in the publication of scientific journals, and is the publisher at the present time of a considerable number of scientific journals of high standing, and they have to do with a number of journals of the type that the association members are interested in. Accordingly, we made a contract, which was signed by the president of the association, to run for five years, with the Williams & Wilkins Co., which I cannot, of course, explain to you here in detail, but, in essence, the contract calls for something like this:

That the association obligates itself to furnish the manuscript in proper shape to print, including the methods as they may appear, and, also, 200 subscriptions, and that the Williams & Wilkins Co. takes charge of the production of the Journal, the mailing, and handling the accounts of the Journal, and that the total cost of the Journal will be in the neighborhood of $3,000 for a volume of 600 pages, to be issued quarterly; that the Williams & Wilkins Co. takes the responsibility for $2,000 of the $3,000, the association taking the responsibility for the balance; that any profits that may arise (moneys taken in above the cost of production) shall be divided equally between the publishers and the association, the publishers basing their charges to the association for the production of the Journal on the cost of production plus 10%, which is to represent a business profit for the handling of the proposition.

Now, there are some other details, but essentially it is that—a contract for 5 years, subject to renewal.

We went to work on that general proposition, it being the most favorable we succeeded in getting from any publisher; in fact, very few of the other publishers were willing to take the same chances and be responsible for any of the cost of producing the Journal.

Now, we went to work on that basis and, as you know, we have issued three numbers of the four that make the first volume, and in those three numbers have been published the proceedings for 1913 and practically the complete proceedings for 1914.

With reference to subscriptions and the financial standing of the Journal at the present time, I am glad to say that I can make a very favorable report. We have up to the present time obtained through the office of the treasurer—that is to say, through my office—over 480 subscribers (that was as of November 1), and there have been obtained through the publishers about 100 subscriptions, so that the number of subscribers to the Journal is somewhat in excess of 600, and the end is not yet, because I still receive in the office of the secretary-treasurer a few subscriptions each month, and the publishers inform me that they are receiving a substantial number of additional subscriptions each month. So there is very little doubt that the subscription list will increase considerably during the coming year. Of course, at the end of this volume it is impossible to say how many will result in cancellations, for the reason that there will undoubtedly be a number of manufacturers who have subscribed to the Journal largely for the purpose of seeing what it was going to be like, and those manufacturers who have no chemists and have subscribed in this fashion will, in some instances, I imagine, cancel their subscriptions. But, on the whole, I think it is safe to predict that in the course of the winter we will add very substantially to the number of our subscribers. I think that to have such a number as 600 subscribers for

a purely scientific journal within less than a year after its first issue is rather an achievement, in which the association is very fortunate.

Now I cannot give you a complete statement of the finances of the Journal at the present time, for the reason that I have not the data that are in the hands of the publisher, and the contract with the publisher does not call for an accounting until the completion of the first volume. I can give you only the data on the business of the Journal that has passed through my office, and in that connection I can say that we have received in the office of the secretary-treasurer moneys for subscriptions to the total of $2,205.90; that we have the cash which was subscribed toward the guaranty fund, and that, of course, has not been touched. Now, if the publishers have about 100 subscriptions, they have taken in from that source between four and five hundred dollars, and they have also secured up to the present time nine pages of advertising, and there are contracts that have been made by the publishers for several additional pages, so that in this number just issued there are 8 or 9 and in the next there should be 10, 11, or 12 pages of advertising. So we can figure, deducting the commissions that have to be paid to the solicitors of the advertising and that have to be paid for the cost of printing, that there are probably four or five hundred dollars in sight from advertising.

Now, inasmuch as the estimated cost of the production of the Journal is a little in excess of $3,000; that is to say, the publishers figure it will cost us $3,000, to which we have to add some slight expense for the business of conducting the Journal through my office, and to which we also have to add certain additional (not very large) sums for corrections and for unforeseen items in connection with the production of the Journal—and, of course, we have to add to that the cost of printing the advertising matter—the cost of producing the Journal will not be very much in excess of $3,000 for 600 pages. We have taken in through my office over $2,200, which, with that received by the publishers for subscriptions and for the advertising, makes it safe to predict that we cannot help breaking even on this first volume of the Journal, with a considerable chance of having a little something left over, which, of course, would be divided between the association and the publishers. So much for the financial status of the Journal.

There is one other thing to be mentioned in that connection, and that is a standard with reference to advertising. The executive committee was very hesitant about the advertising policy of the Journal, and it was only after a great deal of debate that it was decided to accept advertising at all. The contract with the publishers gives the executive committee absolute control over the advertising which shall be accepted. You can see that this is essential. There was no question but that the association could secure a great deal of advertising if they would accept

advertising of an indiscriminate character. But the executive committee felt that that was unwise, and has adopted the policy of accepting the advertising of no concern that produces a product which is subject to any of the laws that any of the members of the association have to enforce, and the executive committee was under the impression that by following that policy—in addition to the policy of decent advertising generally—that we could afford to accept advertising on that basis, and that we probably would not get into any trouble, or allow ourselves to be misrepresented, and that it would be perfectly safe. That, of course, limits the advertising, so far as scientific matters are concerned, to the manufacturers of supplies, analytical instruments, glassware, etc., and publishers of books, and cuts out the advertising of manufacturers of miscellaneous feeds, foods, drugs, and kindred materials which are subject to laws that the members of the association have to enforce.

Now the work of managing the Journal this year has been done entirely by my office; that is to say, all the business arrangements, preparation of manuscript, reading of proof, and everything that goes with the correspondence in connection with the Journal and with reference to the subscribers has been run through my office, and it was done under instructions by the executive committee. Now, it seems to me that the time has come for the association to decide for itself if it is satisfied with the Journal, what the editorial policy of the Journal shall be, and how the Journal shall be run and managed. The editorial work so far has not been difficult, consisting principally in the clerical work of preparing the manuscript, reading the proof, etc., and the handling of subscriptions. Now, the clerical work has dwindled considerably, because the subscriptions are being handled by the publishers. The editorial work up to the present time has been comparatively easy, consisting chiefly of getting the proceedings of the association in shape, and it has been editorial work that has not required chemical judgment or judgment on matters of policy. As long as that is all there is to it, the matter is very simple, but my understanding of the executive committee's ideas concerning the publication of the Journal is that the Journal is to be more than a mere vehicle for the publication of the proceedings and methods; that the Journal is to print papers bearing on methods and official work, and matters of that kind. Now, if that is to be the policy, somebody has got to pass on the papers that are read here in the association and subsequently offered for publication. I am referring to papers of a general nature. We have had a number on the program this time, and undoubtedly we will have others, and undoubtedly the members of the association will from time to time offer manuscripts for publication in the Journal when they think it important to have their material published and without waiting the best part of a year to present it before the association.

Now, as everybody knows, passing on manuscripts, correspondence with authors concerning their manuscripts, and all that is involved in that is not a pleasant job. The people who do it with the best intentions make a lot of others sore and a few enemies. As long as the Journal was simply a medium for the publication of the proceedings of the association it was a simple matter and I could manage it. But we have about come to the point where somebody has got to decide matters of editorial policy—say whether papers shall be printed or not, or abridged, or modified, and I think it is up to the society to name a person for the management of the policies of the Journal if they are satisfied with the Journal in its present shape, and I suggest, Mr. President, that that be made a subject for discussion and such action as the society cares to take.

Mr. Jones suggests that I tell you something about the nature of the subscriptions—of the list of subscribers. You will be interested to know that before the first number appeared we had requests for the Journal from Canada, South America, Australia, and England. I think we have a considerable number from Canada. We haven't, of course, owing to the conditions in Europe, any subscriptions, so far as I know, on Continental Europe. There is no doubt we can get them as soon as peace comes along. Among our subscribers we have a number of men who are manufacturers. I don't know, but I should venture to guess that fully a half of our subscribers are chemists with manufacturing concerns. But I think it is rather gratifying that within three, or four months after the first number appears we should be getting calls from the furthermost corners of the earth.

A board of editors of the Journal, consisting of the secretary as chairman and four members to serve one, two, three, and four years, respectively, each following appointment to be for four years, was authorized by vote of the association.

REPORT OF COMMITTEE A ON THE RECOMMENDATIONS OF REFEREES.

W. W. SKINNER (Bureau of Chemistry, Washington, D. C.), *Chairman.*

(Phosphoric acid, potash, soils, inorganic plant constituents, nitrogen, insecticides, and water.)

PHOSPHORIC ACID.

It is recommended—

(1) That further study of the methods for basic slag be made, with the idea of keeping them before the association until the field committee reports.

Approved.

(2) That work be continued in the investigation of the use of neutral ammonium citrate, sodium citrate, and citric acid solutions in the determination of reverted phosphoric acid in fertilizers, in harmony with the recommendations of the referee on phosphoric acid.

Approved.

POTASH.

It is recommended—

(1) That further coöperative work on the perchlorate method for the determination of potash be discontinued for the present, but the succeeding referee is advised to continue the investigation of the method with a view to perfecting the working details.

Approved.

(2) That the 80% by volume denatured alcohol, formula 1 (U. S. Int. Rev. Reg. No. 30, revised Aug. 22, 1911, p. 45), may be used for washing potassium chloroplatinate.

Approved.

(3) That further work be done on the method for obtaining water-soluble potash to determine whether hydrochloric acid shall or shall not be used before the precipitation with ammonium hydroxid and ammonium oxalate is made.

Approved.

(4) That the work on the availability of potash be continued.

Approved.

SOILS.

It is recommended—

(1) That the following be adopted as provisional for determination of inorganic carbon in soils as a modification of the Marr method (J. Agr. Sci., vol. 3, pt. 2, p. 155):

Place from 5 to 20 grams of soil, depending upon the carbonate content as indicated by a qualitative examination, in a suitable flask or bottle having a capacity of 250 cc. and which will withstand a vacuum of approximately 70 cm. Add 80 cc. carbon-dioxid-free water; after mixing thoroughly connect flask to suitable apparatus provided with condenser and Meyer absorption tube (similar to apparatus described in J. Ind. Eng. Chem., **6**: 561, but omitting Camp absorption tower and substituting Meyer absorption tube). Start suction, and when air has been removed from apparatus add to the contents of flask, through separatory funnel, 20 cc. dilute hydrochloric acid (2 cc. hydrochloric, specific gravity 1.19, to 188 cc. water).

NOTE.—This proportion of hydrochloric acid plus the 80 cc. of water previously added gives a strength of acid for decomposition of carbonates of 2–100. If the nature of the soil is such that a greater strength of acid is considered necessary, an amount of acid can be taken to make the strength of acid used for digesting soil 3–100.

Allow acid to act on soil for from 5 to 15 minutes, continuing suction, before heating contents of flask. Then boil for from 20 to 30 minutes, maintaining a vacuum

of 65 to 70 cm. in the boiling flask. Care should be taken that solution in flask is not drawn up into condenser tube. Absorb carbon dioxid evolved in a suitable quantity of from one-third to one-half saturated barium hydroxid solution, contained in a Meyer absorption tube. The barium carbonate after filtering and washing can be determined either volumetrically or gravimetrically (see article by J. R. Cain, J. Ind. Eng. Chem., 6: 465).

A blank determination must be made under same conditions and correction applied.

Approved.

(2) That further study be made of methods for total sulphur in soils, including a comparison of the following methods: Sodium peroxid fusion; heating soil with magnesium nitrate solution as used for total phosphorus in soils; modification of Eschka's method for sulphur in coal; ignition of soil with mixture of magnesium oxid, sodium carbonate, and ammonium nitrate.

Approved.

(3) That methods for the determination of the total constituents of soils be studied with a view to substituting them for the "strong acid digestion" as outlined under section 5, page 14, U. S. Bureau of Chemistry Bulletin 107. Referred to referee for next year.

Approved.

INORGANIC PLANT CONSTITUENTS.

It is recommended—

(1) That the present official methods for iron, aluminum, calcium, and magnesium be made official only for plant materials other than seeds.

Approved.

(2) That the extension of the official method for iron and aluminum as recommended by the referee in 1913 be made a provisional method for calcium and magnesium in the presence of minute quantities of manganese for plant materials other than seeds.

Approved.

(3) That suitable methods be devised for the determination of iron, aluminum, calcium, and magnesium in the ash from seeds.

Approved.

NITROGEN.

It is recommended—

(1) That the zinc-ferrous sulphate-iron method for nitrates be further studied during the coming year, with a view to final adoption as official in 1916.

Approved.

(2) That the Jones and Street methods for the determination of organic nitrogen activity be further studied during the coming year, with the special purpose in view of improving or modifying the manipulations in

the conduct of each process so as to increase the accuracy of the water-insoluble organic nitrogen determinations; and, in the case of the Jones method, to overcome the difficulties in the distillation with alkaline permanganate, as well as with the residue for digestion from the paper to the flask; and, in the case of the Street method, to overcome the difficulty in the transference of the residue from the paper to the beaker for digestion with permanganate, and also to devise a way of hastening the filtration and washing of the permanganate residue.

Approved.

(3) That the use of sodium sulphate in place of potassium sulphate in the Gunning method and its modifications be studied by the next referee.

Approved.

(4) That the Kjeldahl-Gunning-Arnold method be made official.

Approved.

INSECTICIDES.

It is recommended—

(1) That Method I for total arsenious oxid in Paris green (U. S. Bur. Chem. Bul. 107 (rev.), pp. 25–26), and as modified by the referee on page 157, be discarded.

Approved.

(2) That the distillation method for total arsenic as described on page 158 be adopted as official and designated Method I.

Approved.

(3) That the modified methods of C. C. Hedges and C. M. Smith for the determination of total arsenic as As_2O_3 only in Paris green (Methods III (a) and III (b), p. 158) be published in the Revised Methods of Analysis as tentative methods.

Approved.

(4) That the present official method for the determination of total arsenic in lead arsenate (U. S. Bur. Chem. Bul. 107 (rev.), p. 239) and as modified (Methods I (a) and I (b), p. 163) be published in the Revised Methods of Analysis as tentative methods.

Approved.

(5) That the distillation method as described on p. 171 be made official for the determination of total arsenic in lead arsenate.

Approved.

(6) That Method II for the determination of total arsenic as As_2O_5 only in lead arsenate, pages 163–164 be further studied.

Approved.

(7) That Method III, page 164, for the determination of As_2O_3 only in lead arsenate be changed so as to require a boiling of from 20 to 30

minutes with 5 cc. of concentrated sulphuric acid to each gram of sample, and as so modified be further studied.

Approved.

(8) That the distillation method as described on page 172 be adopted as an official method for the determination of total arsenic in calcium arsenate.

Approved.

(9) That recommendation (6) of this report apply equally to calcium arsenate.

Approved.

(10) That the distillation method as described on page 175 be adopted as official for the determination of total arsenic in zinc arsenite.

Approved.

(11) That Method II, page 175, for the determination of total arsenic in zinc arsenite, be discarded.

Approved.

(12) That recommendation (3) apply equally to zinc arsenite.

Approved.

(13) That recommendation (6) apply equally to zinc arsenite.

Approved.

(14) That Methods I and II for the determination of zinc oxid in zinc arsenite be further studied.

Approved.

(15) That method (b) for the determination of moisture in Bordeaux mixture, Bordeaux-Paris green, and Bordeaux-lead arsenate mixtures, when in the form of pastes as described on page 178 be adopted as official.

Approved.

(16) That the method for the determination of carbon dioxid in Bordeaux mixture, Bordeaux-Paris green, and Bordeaux-lead arsenate as described on page 178 be adopted as official.

Approved.

(17) That the electrolytic method for the determination of copper in Bordeaux mixture as described on page 178 be adopted as an official method.

Approved.

(18) That the thiosulphate titration method for the determination of copper in Bordeaux mixture as described on page 178 be adopted as an official method.

Approved.

(19) That the method for water-soluble arsenious oxid in Bordeaux-Paris green as described on pages 179–180 be adopted as a tentative method.

Approved.

(20) That the distillation method for the determination of total arsenic in Bordeaux-Paris green as described on page 179 be adopted as an official method.

Approved.

(21) That recommendation (3) of this report apply equally to Bordeaux-Paris green.

Approved.

(22) That the electrolytic method for the determination of copper in Bordeaux-lead arsenate as described on page 182 be studied further with reference to its applicability to the determination of copper in both Bordeaux-Paris green and Bordeaux-lead arsenate, particular attention to be given to the effect of the various impurities which may be present in commercial samples.

Approved.

(23) That the thiosulphate titration method for the determination of copper in Bordeaux-Paris green as described on page 178 be further studied.

Approved.

(24) That the method for water-soluble arsenic oxid in Bordeaux-lead arsenate, as described on page 182 be adopted as a tentative method.

Approved.

(25) That the method for the determination of lead oxid in Bordeaux-lead arsenate as described on page 182 be further studied.

Approved.

(26) That the silicotungstic acid method for the determination of nicotin as described on page 183 be adopted as an official method.

Approved.

(27) That the coöperative work on insecticides for next year include a study of the following: (*a*) A method other than an electrolytic one for the separation and determination of copper and lead in a Bordeaux-lead arsenate mixture; (*b*) methods for the determination of the principal ingredients in zinc-arsenic compounds, alone and in combination with Bordeaux mixture.

Approved.

(28) That the methods for the analysis of lime-sulphur solution published in the Journal of the Association of Official Agricultural Chemists, Volume 1, No. 1, as modified and submitted to the committee on revision, be adopted as official with a view to their final adoption in 1916.

Approved.

WATER.

It is recommended—

That the method for the determination of calcium and strontium be adopted as an official method.

Approved.

Dr. Harvey W. Wiley, in a short address, recounted the history of the organization of the association, and congratulated the membership upon the success and enthusiasm of the meeting.

The association adjourned to reassemble at 2.20 o'clock p.m.

TUESDAY—AFTERNOON SESSION.

REPORT OF COMMITTEE B ON THE RECOMMENDATIONS OF REFEREES.

R. E. Stallings (Department of Agriculture, Atlanta, Ga.), *Chairman.*

(Dairy products; feeds and feeding stuffs; sugar; water in foods and feeding stuffs; organic and inorganic phosphorus in foods, feeding stuffs, and drugs; separation of nitrogenous substances in meat products; nitrogenous bodies (milk and cheese); testing chemical reagents; medicinal plants and drugs.)

DAIRY PRODUCTS.

It is recommended—

(1) That the following be adopted as auxiliary provisional methods:

(a) *Sour serum.*—Allow the milk to sour spontaneously, filter, and determine the index of refraction of the clear serum by means of the Zeiss immersion refractometer. A reading below 38.3 indicates added water.

(b) *Ash of sour serum.*—Allow the milk to sour spontaneously and filter. Transfer 25 cc. of this serum to a flat-bottomed platinum dish and evaporate to dryness over the water bath. Then heat the contents of the dish over a small flame (to avoid sputtering) until charred. The dish is then placed in the electric muffle (with pyrometer connected) and ashed at a heat not greater than 500°C. or 900°F. Cool and weigh. Result is expressed in grams per 100 cc. An ash below 0.730 indicates added water.

(c) *Ash of acetic serum.*—Transfer 25 cc. of the serum to a flat-bottomed platinum dish and proceed as directed under "Ash of sour serum." An ash figure below 0.715 grams per 100 cc. indicates added water.

Approved.

(2) That in conjunction with the refraction of the copper, acetic or sour serum, the ash of the sour serum or of the acetic serum be determined in all cases where the indices of refraction fall below the minimum limit. The acetic serum ash multiplied by the factor 1.021 equals the sour serum ash (dilution of the acetic serum being 2%).

Approved.

(3) That further study be made on the Harding-Parkin method for fat determination (J. Ind. Eng. Chem., 1913, **5**: 131), in comparison with the present official and provisional methods.

Approved.

(4) That further study be given to enzym reactions of milk.

Approved.

FEEDS AND FEEDING STUFFS.

It is recommended—

(1) That a further study by collaborators of sulphur dioxid in bleached grains be made.

Approved.

(2) That the method of determining the acidity of corn as specified by Black and Alsberg he considered by the referee next year, with a view to its adoption as an official method, and that the method be studied to see if changes are necessary to make it applicable to other grains than corn.

Approved.

(3) That the referee on crude fiber make a further study on the comparison of the various modifications of the method for the determination of crude fiber.

Approved.

(4) That the following method for the approximate estimation of foreign material, excluding grit, in feeding stuffs be further studied collaboratively with a view to its adoption as a provisional method:

Preparation of sample.—Mix original unground sample thoroughly, quarter, discard diagonally opposite quarters until remaining two quarters weigh 10 grams.

Determination.—Separate the 10-gram sample by means of 20, 30, 40, and 50 mesh sieves. By aid of hand lens or other magnifying instrument, pick out foreign materials; first from finest separation, and the next finest in order until all separations have been examined. Combine foreign materials separated and weigh.

Approved.

(5) That the size of sample of scratch and poultry feeds necessary to get concordant results on quantitative grit determinations be further investigated.

Approved.

(6) That the following recommendation of 1914 be studied during the coming year: That methods for the detection of peat dried at high temperatures in feedstuffs be investigated, and that the maximum percentage of foreign materials permissible in mill by-products be investigated.

Approved.

SUGAR.

It is recommended—

(1) That the study of the modifications of the Clergot method be continued, with special reference to the accurate determination of sucrose in complex mixtures of carbohydrates.

Approved.

(2) That efforts be made toward the adoption of an accurate method for determining small quantities of invert sugar in presence of large

amounts of sucrose. In this connection the colorimetric methods for estimating invert sugar should be examined.

Approved.

(3) That next year's referee, in collaboration with the U. S. Bureau of Chemistry, establish a table of reduction factors for the more common reducing sugars.

Approved.

(4) That the official text of the methods of the International Commission be substituted for the present text on pages 39 and 40 of U. S. Bureau of Chemistry Bulletin 107 (revised), and that these methods of the International Commission be brought up to date.

Approved.

(5) That the following method for preparing a salt-free alumina cream be adopted in place of the present method on page 40:

Concentrated alum solution is precipitated with a slight excess of ammonium hydroxid and the precipitate is washed by decantation with water until the solution is free from sulphates. The excess of water is then poured off and the residual cream is stored in a stoppered bottle.

Adopted.

(6) That on page 41, at the end of section (c), the following be inserted:

For concentrations of sucrose less than 13 grams to 100 cc. of invert solution the following general formula should be used:

$$S = \frac{100\,(P - I)}{142.66 - \frac{t}{2} - 0.0065\left(142.66 - \frac{t}{2} - (P - I)\right)}$$

The above formula is applicable to the determination of sucrose in presence of dextrose, commercial glucose, and all other substances whose optical activity is not affected by the inverting acid. With materials which contain much levulose, such as honey, fruit products, etc., the method gives too high results.

Approved.

(7) That on page 41, at the end of section (d) the following formula be substituted for the present formula for calculating the per cent of sucrose in presence of raffinose:

$$S = \frac{0.5124\,P - I}{0.839}$$

The above formula supposes that the polarizations be made at exactly 20°C. If the temperature (T) be other than 20°C., the following formula should be used:

$$S = \frac{P\,(0.4724 + 0.002\,T) - I}{0.899 - 0.003\,T}.$$

Having calculated S,

$$R = \frac{P - S}{1.852}.$$

Approved.

(8) That after section (d) the following be inserted:

(e) DETERMINATION OF SUCROSE BY MEANS OF INVERTASE—PROVISIONAL.

Preparation of invertase solution, Hudson's method.—Break up 5 pounds of pressed yeast, which may be either baker's or brewer's yeast, add 30 cc. of chloroform to it in a closed flask and allow it to stand at room temperature (20°C.) overnight. By the morning the solid mass will have become fluid, and it should then be filtered through filter paper, allowing several hours for draining. To the filtrate add neutral lead acetate until no further precipitate forms, and again filter. Precipitate the excess of lead from the filtrate with potassium oxalate and filter. To this filtrate add 25 cc. of toluene and dialyze the mixture in a pig's bladder for 2 or 3 days against clear, running, tap water. The dialyzed solution should be colorless, perfectly clear after filtration, and neutral to litmus; it should be preserved in an ice box with the addition of a little toluene to prevent the growth of micro-organisms. The optical activity of the invertase solution is noted and a correction for this, according to the amount of solution used, must be applied to the invert reading.

Determination.—Dissolve the normal weight (26 grams) of substance in water, clarify, make up to volume, and take the direct polarization (P) as under section (d). Remove the excess of lead from the filtrate, if lead has been used as a clarifying agent, with anhydrous sodium carbonate or potassium oxalate, and filter. To 50 cc. of the filtrate in a 100 cc. flask add acetic acid by drops until the reaction is acid to litmus, add 10 cc. of the stock invertase solution, and let stand in a warm place (about 40°C.) overnight. Cool and make up to 100 cc. at 20°C. Polarize at 20°C. in a 200 mm. tube. Allow the solution to remain in the tube for an hour and repeat the polarization. If there is no change from the previous reading the inversion is complete; then the reading and temperature of the solution are carefully noted. The reading is corrected for the optical activity of the invertase solution and then multiplied by 2. The percentage of sucrose is then calculated by the following formula:

$$S = \frac{100\,(P - I)}{142 - \frac{t}{2} - 0.0065\left(142 - \frac{t}{2} - (P - I)\right)}$$

S = per cent of sucrose.
P = direct reading.
I = invert reading.
t = temperature at which invert reading is made.

Approved.

(9) That on page 51 before section (c) the following be inserted:

Reducing sugars other than dextrose may be determined, using Allihn's modification of Fehling's solution, by means of the above table and method by use of the following factors:

Arabinose	= glucose × 0.969
Xylose	= glucose × 1.017
Levulose	= glucose × 1.093
Invert sugar	= glucose × 1.046
Galactose	= glucose × 1.114

Approved.

(10) That on page 67, before section "3. Ash," the table for specific gravity and total solids of sucrose solutions at $\frac{20°}{4°}$ used by the U. S. Bureau of Standards and Reichsanstalt of Germany be inserted.

Approved.

(11) That on pages 243 to 251, in the Munson and Walker table for calculating lactose, the column for lactose with one-half molecule of water be omitted.

Approved.

WATER IN FOODS AND FEEDING STUFFS.

It is recommended—

(1) That the method of drying in a vacuum without heat as outlined below be adopted as a provisional method:

Mix the sample thoroughly and weigh about 2 to 5 grams by difference from a stoppered weighing bottle into tared crucibles provided with covers which are tared with crucibles. Where subsequent fat determinations are to be made, the fat extraction cones may be used. Substances that dry down to horn-like material should be mixed with fat-free cotton or other suitable material (previously tared with the container). Place 200 cc. of fresh C. P. sulphuric acid in a good 6-inch vacuum desiccator. Put triplicate samples in separate desiccators, smear the edges of the latter and the stop-cock with lubricant (a mixture of 3 parts of hard paraffin and 5 parts of vaseline is suggested) and exhaust as completely as possible by means of a vacuum pump. If a pump is not available, place 10 cc. of ether contained in a small beaker into the desiccator, and exhaust with a water filter pump. It will be found convenient to interpose between the pump and the desiccator an empty bottle next to the desiccator and a bottle of water following this. Draw the air from the desiccator through the water and turn the desiccator stop-cock at just the instant when the water begins to rise in the tube leading from the empty bottle. Gently rotate the desiccator four or five times during the first 12 hours to mix the sulphuric acid with the water which has collected as an upper layer. At the end of 24 hours open the desiccator, forcing the incoming air to bubble through C. P. sulphuric acid. If a good vacuum has been maintained, the samples are ready for the first weighing. After weighing, place in a desiccator with fresh C. P. sulphuric acid and exhaust as before. Rotate the desiccator several times during the interval and weigh again at the end of 24 hours, repeating this process of drying in vacuo over sulphuric acid until the weight is constant.

Adopted.

ORGANIC AND INORGANIC PHOSPHORUS IN FOODS, FEEDING STUFFS, AND DRUGS.

It is recommended—

That final action be deferred until 1916 on the magnesia mixture method of E. B. Forbes for the determination of water-soluble inorganic phosphorus in animal substances.

Approved.

SEPARATION OF NITROGENOUS SUBSTANCES IN MEAT PRODUCTS.

It is recommended—

That the referee for next year attempt to determine the relative amounts of some of the dissociation products in water-soluble and water-insoluble meat proteins.

Approved.

NITROGENOUS BODIES (MILK AND CHEESE).

It is recommended—

That study be continued leading to the adoption of methods for the determination of the noncasein proteins and the products of protein decomposition in milk.

Approved.

TESTING CHEMICAL REAGENTS.

It is recommended—

(1) That chemical reagents labeled "U. S. P." shall be tested according to the specifications of the U. S. Pharmacopœia, volume 9 (rev., 1916).

Approved.

(2) The referee recommends that all other chemical reagents be tested according to Chemical Reagents, Their Purity and Tests (2d ed., rev. 1914), by Henry Schenck. The committee recommends that this be not adopted.

Committee's position approved.

(3) That the method for the determination of ethyl alcohol in pharmaceutical preparations as outlined by the referee be studied collaboratively.

Approved.

MEDICINAL PLANTS AND DRUGS.

It is recommended—

(1) That the work on medicated soft drinks, especially the methods for estimating phosphoric acid and glycerin be continued.

Approved.

(2) That the methods named below be printed, so as to be available for study before final adoption.

For the estimation of caffein and acetanilid in mixtures, as given in this year's report;

For the estimation of caffein and acetphenetidin (phenacetin) in mixtures;

For the estimation of caffein and antipyrin in mixtures (J. Ind. Eng. Chem. 1915, **7**: 519);

For the estimation of acetanilid and acetphenetidin (phenacetin) in admixture (J. Ind. Eng. Chem., 1914, **6**: 665);

For the estimation of acetphenetidin (phenacetin) and salol in mixtures (J. Ind. Eng. Chem., 1915, **7**: 681–684);

For the estimation of acetanilid and sodium salicylate in mixtures;

For the estimation of caffein, acetanilid, and quinin sulphate in mixtures;

For the estimation of caffein, acetanilid, and codein sulphate in mixtures;

For the estimation of caffein, acetanilid, quinin sulphate, and morphin sulphate in mixtures;

For the evaluation of gum tragacanth (J. Ind. Eng. Chem., 1915, **4**: 374).

Approved for printing with report of the editing committee, with a view to their final adoption as provisional methods in 1916.

(3) That the work on pepsin be continued, and that work on papian be taken up also.

Approved.

(4) That the referee on balsam be continued, and that a study be made of the methods of demonstrating the difference between the natural and the artificial product.

Approved.

(5) That in conducting assays for strychnin, reliance be placed on a gravimetric determination and not on one obtained by volumetric means; that another year be devoted to the study of methods for determining strychnin in tablets with a view to incorporating further details which may improve the description of the process in such a way that individuals will be able to obtain more concordant results; and that the study of the determination of strychnin be extended to more complex mixtures.

Approved.

(6) That work on mixtures containing synthetic products be continued.

Approved.

(7) That work on medicinal plants be continued.

Approved.

REPORT OF COMMITTEE C ON THE RECOMMENDATIONS OF REFEREES.

H. E. BARNARD (State Board of Health, Indianapolis, Ind.), *Chairman.*

(Food adulteration)

COLORS.

It is recommended—

That the methods given in the accompanying draft be approved for publication, with the recommendation that they be considered for provisional adoption in 1916.

Approved.

Methods for the Detection and Identification of Coloring Matters in Food Products.

(1) General statements.

The coloring matters used in food products may be divided, although not sharply, into two classes: First, pigments such as ultramarine and lampblack insoluble in the common solvents; second, soluble coloring matters. In the latter class are also included the lakes, etc., readily decomposed with the formation of soluble coloring matters by means of the common reagents.

(2) Detection and identification of insoluble pigments.

These are most commonly used as facings and may often be separated in a condition of more or less purity by washing and allowing the mixture to settle. They must be recognized in general by the microscopic examination and by treatment of the material or the purified coloring matter with reagents. For example, ultramarine is unchanged by alkalies, instantly decolorized by dilute hydrochloric acid with liberation of hydrogen sulphid that may often be detected with lead acetate paper. A large proportion of the common pigments other then lakes are derivatives of the heavy metals, as the yellow, brown, and red ochers and umbers containing iron and perhaps manganese; and various green copper compounds, among which may be included the green chlorophyll derivatives.

(3) Detection and identification of soluble coloring matters and their lakes

This class may be divided for convenience into coal-tar dyes and natural coloring matters. Immiscible solvents must usually be used for the separation of these coloring substances from food products in a condition sufficiently pure for identification. A shorter test for coal-tar dyes sufficient in many cases consists in boiling with wool as described below.

Wool dyeing test.[2]

(a) *Wines, fruit juices, distilled liquors, flavoring extracts, vinegars, beers, sirups' nonalcoholic beverages, and similar products.*—Dilute 20 to 200 cc. of the sample with from 1 to 3 volumes of water and boil or warm on the steam bath with a small piece of white woolen cloth (nun's veiling). When the mixture contains much alcohol continue the warming until most of this has been removed; in other cases take out the wool after 5 to 15 minutes and rinse with water. Then treat the liquid with 3 to 4 drops concentrated hydrochloric acid for each 100 cc. (the reaction must be strongly acid to methyl orange) and warm again for 10 to 20 minutes with a clean piece of wool. The basic dyes go on the fiber best from neutral or faintly ammoniacal solutions and if present will appear on the first piece of wool. Acid colors dye from neutral solutions, but more readily from those containing free acid. If the wool takes up any considerable amount of coloring matter in either case the presence of coal-tar dyes is indicated. The lichen colors[3] (archil, cudbear, litmus) readily go on wool, however, and many other natural colors, as turmeric, will dye the fiber,

---

[1] Useful analytical properties of all these insoluble coloring matters are described in G. Schultz's Farbstofftabellen, 1912, and in other standard works.

[2] See Strohmer, Z. anal. Chem., 1885, **24**: 625; Arata, ibid., 1889, **28**: 639; Winton, Conn. Agr. Exper. Sta. Rept., 1899, pt. 2, p. 131.

[3] Tolman. J. Am. Chem. Soc., 1905, **27**: 25.

if present in considerable amount. On the other hand, a few coal-tar dyes, especially auramine O and naphthol green B, are quite unstable and if present in small amounts may give no distinct dyeing. Acid dyes are much more frequently used than basic ones and may in most cases be removed from wool without much decomposition by "stripping" the latter with dilute ammonia,[1] while by the action of the alkali many of the natural colors are destroyed and some of the others remain for the most part on the fiber. If the behavior with wool in neutral and in acid solution has indicated the presence of acid dyes, thoroughly rinse the colored cloth, cover it in a casserole with dilute ammonium hydroxid solution (about 2%) and boil for a few minutes, remove the cloth, and squeeze out the adhering liquid. Boil the ammoniacal solution a few minutes longer to remove excess of ammonia, drop in a piece of clean wool previously well wetted, make distinctly but not strongly acid with hydrochloric acid, and boil again. If acid coal-tar dyes are present they will usually give a fairly clean, bright dyeing on this second piece of wool. A further purification may be carried out by repeating the stripping and redyeing, though generally accompanied by corresponding loss of dye.

(b) *Candies and similar colored sugar products.*—Dissolve about 20 grams of the sample in 100 cc. of water and treat the solution as described under (a). When the coloring matter is on the surface of the candies, the solution should be poured off before the colorless inner portion has dissolved, thus avoiding the presence of an unnecessarily large amount of sugar.

(c) *Jams and jellies.*—Boil a mixture of 10 to 20 grams of the sample and 100 cc. of water with wool in neutral and also in acid solution as described under (a). For thick jams, however, it is usually better, though less easy, first to extract the coloring substances, treating the product as dissolved below under (d).

(d) *Canned and preserved fruits and vegetables, sausage casings, smoked fish, coffee, spices, etc.*—Macerate 20 to 200 grams of the sample with 4 to 5 times its weight of 80% alcohol. After standing a few hours pour off the solvent as completely as possible and repeat the extraction, using 70% alcohol containing about 1% of ammonia. The filtered alcoholic extracts may be examined separately, but it is easier to boil the ammoniacal solution until practically neutral, completing the neutralization with a small drop of acetic acid. The neutral extract (80% alcohol) is now added and the evaporation continued until most of the alcohol is removed. The solution, or a portion of it, is now ready to boil with wool as described under (a).

(e) *Cocoa and chocolate products.*—Treat cocoa as described under (d). However, alcoholic extract will contain a large amount of natural coloring matter and several dyeings and strippings may be necessary to get rid of this and show the presence of coal-tar dyes. Chocolate may be treated similarly, but it is better to proceed as follows:

Wash 20 to 200 grams of the well-divided sample with gasoline on a filter until most of the fat has been removed; if the gasoline is colored it is reserved and examined for oil-soluble dyes as given under (g). The residue, after the removal of most of the adherent solvent by evaporation or pressure between layers of absorbent paper, is digested with alcohol, following the procedure given under (d). Chocolate and cocoa products may also be mixed directly with 3 to 4 times their weight of hot water and the magma boiled with wool at once, as stated under (a), though because of the large amount of fatty and proteid materials, the plan is not very satisfactory.

(f) *Wheat and rye products, macaroni, etc.*—Proceed as given under (d), except that it is advisable in most cases to work with a large amount of the sample, 200 to 500 grams, and a smaller amount of alcohol, relatively. Where only the acid dyes are to be tested for, the extraction with neutral 80% alcohol may be omitted with advantage.

[1] Sostegni and Carpentieri. Z. anal. Chem., 1896, **35**: 397.

(g) *Fats and oils.*—For the separation of the coloring matter use one of the following methods:[1]

(1) Shake the oil or melted fat with an equal volume of 90% alcohol. The alcohol after separation will contain aniline yellow, aminoazotoluene, and auramine, if these are present.

(2) Saponify 20 to 200 grams of the oil or fat with alcoholic potash, and after removal of most of the alcohol on the steam bath extract the soap with ether or gasoline. Most of the common dyes are removed by this treatment, though the digestion with strong alkali may cause some decomposition and the extraction is rather troublesome.

(3) Dilute 20 to 200 grams of the oil or melted fat with 1 to 2 volumes of gasoline and shake out successively with the following reagents: Dilute potassium or sodium hydroxid solution 2 to 4%; hydrochloric acid 12 to 15%; phosphoric-sulphuric acid mixture consisting of 85% phosphoric acid to which has been added about 10 to 20% by volume concentrated sulphuric acid.

The dilute alkali extracts Sudan G (also annatto). Aniline yellow (7), aminoazotoluene, and butter yellow (16) are taken out by the dilute acid, the first two forming orange-red, the latter cherry-red solutions in this solvent. Benzeneazo-B-naphthylamine and homologues also come in this group, though they are not very readily extracted and rapidly decompose on standing in strongly acid solution. The phosphoric-acid mixture is necessary for the extraction of Sudan I No. 11, Sudan II No. 43, Sudan III No. 143, and the homologue of the last, Sudan IV. The procedure is not very suitable in presence of auramine, but this dye is seldom found in oils. The solutions in alkali and dilute hydrochloric acid are neutralized, that in the phosphoric-acid mixture diluted somewhat and partially neutralized, the liquid being cooled by holding under the tap or by adding a little ice. The dyes in fairly pure condition are now extracted by shaking with ether or gasoline.

For the dyeing test the alcoholic solutions obtained by method (1) is used directly. The ether or gasoline solutions obtained by methods (2) and (3) are evaporated to dryness and the residues dissolved in 10 to 20 cc. of strong alcohol. To the alcoholic solution add some strands of white silk and a little water and evaporate on the steam bath until the alcohol has been removed or until the dye is taken up by the silk. The dyeing test is sometimes unsatisfactory, and in all cases a small portion of the alcoholic solution should be tested by treating with an equal volume of concentrated hydrochloric acid and adding stannous chlorid. The common oil-soluble coal-tar dyes are rendered redder or bluer by the acid and decolorized by the reducing agent. Most of the natural coloring matters become slightly paler with the acid; little changed by the stannous chlorid.

Separation of soluble coloring matters in pure condition.

Mixtures of dyes must be separated in general by means of immisicible solvents or by precipitants.[2] Although in many cases immisicible organic solvents may

[1] Doolittle, U. S. Bur. Chem. Bul. 65, p. 152; Frehse, Ann. fals., 1910, **3**: 293; Berry, U. S. Bur. Chem. Circ. 25; Loomis, U. S. Bur. Chem. Circ. 63; Gruenhut, Chem. Zentr., 1898, (2) 943.

[2] Berry, U. S. Bur. Chem. Circ. 25; Loomis, U. S. Bur. Chem. Circ. 63; Seeker, Dreaper, Feilmann, Hewitt, Gardner, Allen's Commercial Organic Analysis, 4th ed., vol. 5; Leach, Food Inspection and Analysis; Price, U. S. Dept. Agr., B. A. I. Circ. 180. For fruit colors see Girard and Dupré, Analyse des Matières Alimentaires, etc.; also Tolman, U. S. Bur. Chem. Bul. 107 (1908), p. 192; and Truchon and Martin-Claude, J. pharm. chim., 1901, **13**: 174.

be used directly for the extraction of coloring matters from solid food products, it is advisable usually to first separate the coloring substances from the bulk of water-insoluble material, obtaining it finally in aqueous solution as free as possible from suspended matter, alcohol, acids, alkalies, and salts. For this purpose proceed as described under the method for dyeing on wool, the solution being the same as that employed in boiling with the fiber.

The employment of immiscible solvents for the separation of mixtures of coloring matters must usually take the form of a systematic fractionation[1] as many of the dyes used do not differ very greatly in their solubilities in the available liquids. When it seems probable that only the seven coal-tar dyes permitted by United States Department of Agriculture Food Inspection Decision No. 76 are present, the following abridged procedure may be used for their separation:

The solution containing the coloring matter[2] is treated with one-half its volume concentrated hydrochloric acid and extracted a few times with amyl alcohol. The alcohol extracts are combined, then washed with four or five portions of N/4 hydrochloric acid or until this solvent extracts very little color. These washings will contain any indigo carmine and amaranth present, the former dye being removed somewhat more readily than the latter. With ordinary concentration very little ponceau will be removed.

The amyl alcohol is then measured; if necessary, treated with an equal volume of petroleum ether or low boiling point gasoline, and again washed several times with N/4 hydrochloric acid to extract ponceau 3R and naphthol yellow S. Or without dilution with gasoline it may be washed with 5% salt solution until these two dyes are taken out. The ponceau and yellow being removed, the amyl alcohol containing an equal volume of gasoline is washed a few times with water, which will extract orange I. This dye having been removed, the solution, although appearing almost colorless, perhaps, is shaken out with very dilute caustic soda solution to remove erythrosine. If considerable orange I is present, some of it may contaminate the washings containing the ponceau 3R and naphthol yellow S, especially when these have been separated by means of N/4 hydrochloric acid after addition of gasoline.

If indigo carmine and amaranth are both present, it will be shown by the appearance of the N/4 hydrochloric acid washings of the amyl alcohol. Instead of attempting to separate them by fractionation, it is best to destroy the indigo carmine in one portion by adding a few decigrams of urea and a drop or two of normal sodium nitrite solution, then warming. From another portion, amaranth is removed by dropping in a few particles of sodium hydrosulphite ($Na_2S_2O_4$) until colorless, then shaking with air until the blue has returned.

The N/4 acid solution (or the salt solution) containing the ponceau and naphthol yellow S is treated with enough hydrochloric acid to make it about double normal and shaken out a few times with washed ethyl acetate.[3] From the combined ethyl acetate extracts, the yellow is removed by shaking out with water. It must always be remembered that naphthol yellow S is almost colorless in strongly acid solutions, and its absence in washings, etc., must never be assumed until these have been made alkaline. The ponceau 3R is finally separated from the acid solution by shaking this with amyl alcohol, then washing out the dye from this extract with a few small

[1] Mathewson, J. Ind. Eng. Chem., 1913, **5**: 26; U. S. Bur. Chem. Circs. 89, 113.

[2] The concentration of the dye solution should be not greatly different from 0.05% to 0.01%. The solutions obtained in the examination of colored food products practically never require further dilution, but with commercial food colors care must be taken that the concentration is not too high.

[3] Used instead of amyl acetate, as suggested by Loomis, Proc. Assoc. Off. Agr. Chem. 1912, p. 57.

portions of water. When (with mixtures containing orange I) the washings of the ethyl acetate, which should contain only naphthol yellow S, become redder with alkalies, they should be combined, made fourth normal with hydrochloric acid, and the contaminating orange removed by shaking out with amyl alcohol-gasoline mixture (1: 1), or they may be treated with one-fifth volume concentrated hydrochloric acid, the dyes extracted by shaking once with amyl alcohol, and from this solution the yellow removed by washing with several portions of 5% salt solution.

The original mixture from which the six colors described were separated by adding acid and shaking out with amyl alcohol may still contain light green SF yellowish, which will be colorless or nearly so in the acid solution. To separate this dye the mixture is treated with strong ammonia or potassium hydroxid solution, until slightly alkaline, then neutralized with acetic acid. Any green present will now be apparent by the color of the mixture, and it may be extracted by shaking with a few small portions of dichlorhydrin. The dichlorhydrin extract, after washing with a little water, is diluted with several volumes benzol or carbon tetrachlorid, and the dye taken out with water.

If other coal-tar dyes are present the solutions obtained in this procedure will not be found to contain a coloring matter corresponding exactly in properties to one of the dyes named above. When coal-tar dyes other than the seven just named are present, reference should be made to the larger works.[1]

Most basic dyes may be separated from mixtures by making alkaline with sodium hydroxid and shaking with ether.[2] The ether (which may or may not be colored) is separated and shaken with 2 to 5% acetic acid, which will take up any dye present, forming a colored solution. Although the common basic colors undergo some alteration by this treatment,[3] it may be used for the qualitative detection and separation of methyl violet No. 451, fuchsine No. 448, Bismarck brown No. 197, malachite green No. 427, and rhodamine B No. 504. With care auramine O may also be separated in this way, though it is quickly decomposed by standing in alkaline solution.

The following short procedure is often convenient for the examination of mixtures of acid dyes. Make the dye solutions[4] strongly acid by adding one-half its volume of concentrated hydrochloric acid and shake with amyl alcohol. Separate the amyl alcohol solution and wash it by shaking with successive portions of water (perhaps one-half volume each) reserving those in separate test tubes or beakers. Because of the acid dissolved in the amyl alcohol, these washings will show a regular decrease in acidity, and the coloring matters of different solubility will appear to be *in maximum* amount in different fractions. Ponceau 6R No. 108 washes out chiefly while the acidity is still high, normal or above. Amaranth No. 107, brilliant scarlet No. 106, and tartrazine No. 94 appear between N/1 and N/4; orange G No. 14 and soluble blue No. 480 between N/2 and N/4; palatine scarlet No. 53, ponceau 2R and 3R No. 55 and No. 56, naphthol yellow S No. 4, cochineal No. 706, crystal ponceau No. 64, and azorubime No. 103, between N/16 and N/256. When the acid is practically all removed orange I No. 85, orange II No. 86, and croecine orange No. 86 begin to wash out, and, less readily, orange IV No. 88, and metanil yellow No. 95. Finally, the unsulphonated coloring matters, as erythrosine J No. 516, erythrosine B No. 517, and the rose bengales No. 520 and No. 523 are removed by water

[1] Heumann, Die Anilinfarben; Schultz, Julius, Green, Organic Colouring Matters; Schultz, Farbstofftabellen; Allen, Commercial Organic Analysis; Milliken, Identification of Pure Organic Compounds, etc.

[2] O. N. Witt, Z. anal. Chem., 1887, **26**: 100; E. Weingärtner, ibid., 1888, **27**: 232.

[3] Kohrmann, Havas and Grandmougin, Ber., 1913, **46**: 2131; also 1914, **47**: 1881.

[4] See footnote on page 76, concerning dye concentrations.

very slowly or not at all when all traces of acid have been taken out. Acid yellow No. 8 and brilliant yellow S No. 86 are not very uniform in composition. They are partially taken up by amyl alcohol from acid solution and appear chiefly in the first washings. Indigo carmine No. 692 behaves somewhat similarly.

The natural coloring matters as a class show much less tendency to dye animal fiber than do the common synthetic colors. In many cases the crude products used contain a number of colored substances, and a complete separation can scarcely be attempted. Most of the natural coloring matters, in dilute solution, are sensitive to alkalies, some of them sensitive to acids, so such reagents must be used with care. The following properties are useful in dealing with mixtures of natural colors.

Ether extracts from neutral solutions, carotin and xanthophyll, the pigments found in leaves, fats and oils, egg yolk, carrots, etc. Similar or identical coloring matters are those of tomatoes and paprika. The green chlorophylls are also extracted. These coloring matters are not removed from the ether by washing with dilute alkali, although they may suffer change by action of this reagent.

The coloring matters of alkanet, annatto, turmeric, and of the red dye woods—sandalwood, camwood, and barwood—are very readily and completely extracted by ether from slightly acid solutions. The flavone coloring matters of fustic, of Persian berries (after hydrolysis), and quercitron are taken up in very large proportion by ether from slightly acid solutions; also the coloring matter of Brazil wood, and the green derivatives formed from chlorophyll by alkali treatment.

The coloring matters of logwood, of archil, of saffron, and of cochineal are extracted in relatively small amount by ether from slightly acid solutions, but are largely taken up by amyl alcohol. Caramel, and the anthocyans constituting the red coloring matters of most common fruits, are extracted in relatively small proportion by amyl alcohol from acid solutions. From ammoniacal cochineal (carmine) the ordinary coloring matter is readily reformed by standing with hydrochloric acid.

When cochineal is suspected it is most quickly separated in fairly pure condition by acidifying the mixture with hydrochloric acid with one-third its volume of concentrated hydrochloric acid and shaking with amyl alcohol. The amyl alcohol solution of the coloring matter is washed two to four times with equal volumes of water to remove most of the hydrochloric acid, etc., then diluted with 1 to 2 volumes of gasoline and shaken with a few small portions of water, which will remove the color. This aqueous solution is suitable for the tests with uranium acetate, sodium hydroxid, etc., although, as the green coloration with uranium salts is not developed in the presence of much free acid, it is well to add a little sodium acetate before making this test; or a corrrespondingly large amount of uranium acetate must be added.

Identification of the coloring matter present.[1]

The most widely used of these refer to the color changes produced with acids and alkalies. The behavior with reducing agents, followed, perhaps, by treatment with oxidants or by separation and identification of the reduction products;[2] is of very general application. Tests based on oxidation of the coloring matter and further treatment of the substances formed are also of rather general utility.[3] For

[1] The following references indicate some of the better known general procedures: Witt, Z. anal. Chem., 1887, **26**: 100 (from Chem. Ind., **9**: 1); Weingärtner, Z. anal. Chem., 1888, **27**: 232; Rota, Chem. Ztg., 1898, p. 437; Green, J. Soc. Dyers and Colorists, 1893; Green, Yeoman and Jones, ibid., 1905, **9**: 236; Green, Identification of Dyestuffs, Seeds, 1913; Loomis, U. S. Bur. Chem. Circ. 63.

[2] O. N. Witt. Ber. 1888, **21**: 3471.

[3] Mathewson. U. S. Bur. Chem. Circ. 114.

the spectroscopic methods, consult especially Formanek, Spectralanalyze, and Formanek and Grandmougin, "Untersuchung und Nachweis Organischer Farbstoffe auf Spectroskopische Wege."

For the coal-tar dyes the behavior with acids and alkalies may be judged by moistening pieces of the dyes fiber with the respective reagents. In this test care should be taken that the final dyeing be made in a solution fairly free from foreign matter, as sugar, aromatic substances, etc., adhering to the fiber may modify the reactions. In most cases the amount of dye available is small, and it should not be dyed on too large a piece of wool (or silk). The table following shows the color changes produced by concentrated hydrochloric and sulphuric acids, 10% sodium hydroxid, and 12% ammonia solutions on wool dyed with 0.1 to 0.5% of the respective coloring matters. Included are also the reactions of the oil-soluble colors (designated by O), but these refer to dyeings on silk. The dyes are arranged approximately according to hue. Brown is classed with orange, black (gray) with violet. The numbers given are those used in the work entitled "A Systematic Survey of the Organic Coloring Matters, by Arthur Green, based on the German of Schultz and Julius."

For very many coloring matters the hue in acid or in alkaline solution varies markedly with the concentration of the reagents, and the unknown dye may be compared with solutions of known colors made to approximately the same dye concentration as shown by their appearance. Equal volumes of these solutions are treated side by side with successive portions of acid or alkali of suitable strength.

The seven coal-tar dyes permitted by the United States Department of Agriculture Food Inspection Decision No. 76, are sufficiently characterized in most cases by the solubilities shown in their separation and by the color changes given by acids and alkalies on the dyed fiber (or solution). This is especially true with amaranth and orange I. With the others, the following properties are quite characteristic and should be noted. Indigo carmine is extracted in small proportions from slightly acid solutions by shaking with dichlorhydrin. Most of the other common bluish dyes are triphenylmethane derivatives and are relatively more soluble in this liquid than in the aqueous layer. A small portion of the solution (1 cc.) obtained in the separation may be used directly. Ponceau 3R gives in neutral or faintly acid solutions a bluish red, flocculent precipitate with barium chlorid or acetate, practically all of the dye being removed from solution. Some of the solution obtained in the separation may be used in this test, first neutralizing the free hydrochloric acid with sodium acetate; or, better, it may be evaporated to dryness on the steam bath to remove the acid and the residue taken up with a little water. The solution should contain 0.005% or more of the dye. Naphthol yellow S in solutions containing an excess of ammonia or sodium carbonate becomes intensely rose-red on addition of sodium hydrosulphite ($Na_2S_2O_4$) the color gradually fading again as complete reduction takes place. Erythrosine differs from all other common dyes except the more bluish rose bengales by containing iodin. To test for this, acidify the solution with sulphuric acid, shake with ether, separate the ether solution of the color, and evaporate it to dryness in a platinum dish after adding a few drops of sodium carbonate solution or sufficient of this to form the deep red sodium salt. Hold the dish containing the residue in the Bunsen flame until organic matter is destroyed, take up the residue with water, acidify with sulphuric acid, and test for iodin in one of the usual ways as with chlorin water and carbon disulphid or tetrachlorid, or with starch paste and an oxidizing agent. It is useless to test for iodin with very small amounts of dye, but in most cases sufficient coloring matter can be separated from the food product to give satisfactory results.

Table showing color changes produced by various solutions on wool dyed with 0.1 to 0.5 % of the respective coloring matters.

COLORING MATTER	GSJ NO.	HYDROCHLORIC ACID	SULPHURIC ACID	SODIUM HYDROXID SOLUTION	AMMONIUM HYDROXID SOLUTION
Rhodamine B	504	Orange	Yellow	Bluer	Bluer
Rose bengale	523	Almost decolorized	Orange	No change	No change
Archil	710	Red	Dull brown	Violet	Violet
Magenta	448	Yellowish brown	Do.	Decolorized	Paler
Acid magenta	462	Almost decolorized	Yellow	Do.	Decolorized
Palatine red	62	Darker	Violet	Dull brown	Little change
Bordeaux B	65	Violet	Blue	Brown	Do.
Amaranth	107	Slightly darker	Violet to brownish	Dull brownish	Do.
Azorubine A	103	Little change	Violet	Red	Red
Erythrosine	517	Orange yellow	Orange yellow	No change	No change
Ponceau 6R B	169	Blue	Blue	Dull violet red	Little change
Ponceau 6R	108	Violet red	Violet	Brown	Orange red
Crystal ponceau	64	Do.	Do.	Dull brown	Little change
Ponceau 3R	56	Little change	Little change	Dull orange	Do.
Sudan III (O)	143	Violet, then brown	Green	Violet red	Do.
Safranine	584	Greenish blue	Do.	Red	Red
New coccine	106	Red	Violet red	Yellowish brown	Orange red
Ponceau 2R	55	Little change	Little change	Brownish yellow	No change
Palatine scarlet	53	Darker	Violet red	Do.	Do.
Erythrosine G	516	Yellow orange	Yellow orange	No change	Do.
Sudan II (O)	49	Red	Violet red	Little change	Do.
Sudan I (O)	11	Orange red	Red	Redder	Little change
Cochineal	706	Little change	Little change	Violet red	Violet red
Bismarck brown	197	Redder, darker	Browner	Yellower	Yellower
Bismarck brown R	201	Do.	Do.	Do.	Do.
Orange I	85	Violet	Violet	Red, dark	Red, dark
Orange II	86	Red	Red	Dull red	No change
Croceïne orange	13	Orange red	Orange	Slightly darker	Do.
Orange G	14	Little change	Do.	Dull brownish red	Do.
Orthotoluene-azobeta-naphthylamine (O)	...	Red	Violet	Little change	Do.
Sudan G (O)	10	Orange yellow	Brownish yellow	Orange yellow	Do.
Butter yellow (O)	16	Violet red	Orange yellow	No change	Do.
Aniline yellow (O)	7	Brownish red	Do.	Little change	Do.
Aminoazo-ortho-toluene (O)	...	Dull orange	Do.	Do.	Do.
Fluoresceïne	510	Little change	Little change	Green fluorescent	Green fluorescent

Table showing color changes produced by various solutions on wool dyed with 0.1 to 0.5 % of the respective coloring matters—Continued.

COLORING MATTER	GSJ NO.	HYDROCHLORIC ACID	SULPHURIC ACID	SODIUM HYDROXID SOLUTION	AMMONIUM HYDROXID SOLUTION
Metanil yellow	95	Violet red	Violet	No change	No change
Azoflavine	92	Do.	Violet red	Dull brown	Little change
Fast yellow G	8	Red	Orange	Little change	No change
Brilliant yellow S (O)	89	Violet red	Violet red	Do.	Little change
Tartrazine	94	Slightly darker	Slightly darker	Do.	Do.
Naphthol yellow S	4	Almost decolorized	Very pale dull brown	No change	No change
Auramine	425	Decolorized	Almost decolorized	Decolorized	Paler
Turmeric	707	Red	Reddish brown	Orange	Orange
Quinoline yellow	667	Slightly darker	Brownish yellow	Slightly paler	Little change
Naphthol green B	398	Yellowish	Do.	No change	No change
Guinea green B	433	Pale orange yellow	Pale dull yellow	Decolorized	Decolorized
Light green SF Y	435	Do.	Do.	Do.	Do.
Night green 2B	438	Do.	Do.	Do.	Paler
Malachite green	427	Almost decolorized	Almost decolorized	Do.	Decolorized
Erioglaucine A	436	Yellow	Pale dull yellow or brown	Slightly darker	Little change
Patent blue A	442	Pale orange yellow	Do.	Little change	Do.
Soluble blue	480	Paler	Brown	Pale reddish	Almost decolorized
Indigo carmine	692	Slightly darker	Sligbtly darker	Greenish yellow	Greenish blue
Formyl violet	468	Pale orange yellow	Pale dull orange	Decolorized	Decolorized
Methyl violet	451	Yellowish	Yellowish	Do.	Amost decolorized
Nigrosine, soluble	602	Dull bluish	Dull greenish	Brownish red, paler	Pale reddish

By treatment with reducing agents, as stannous chlorid, titanous chlorid, zinc dust, and sodium hydrosulphite in acid solution, indigo carmine, amaranth, ponceau 3R, and orange I are decolorized. With the indigo carmine the color returns on shaking with air, most readily on warming, or on addition of oxidizing agents, as ferric chlorid or potassium persulphate. Excess of the reducing agents, of course, must be avoided. With the three last-named dyes the color is not restored. Dilute solutions of light green SF yellowish, naphthol yellow S, and erythrosine become paler or colorless with acids, so that the effects of acid reducing agents are not so readily apparent. Neutral solutions of naphthol yellow S are decolorized by sodium hydrosulphite ($Na_2S_2O_4$) and ether reducing agents, the color not returning with air or oxidants. An evanescent deepening of the shade may take place immediately on the addition of the hydrosulphite. Erythrosine and light green SF yellowish become paler with sodium hydrosulphite, the color being partially restored on addition of potassium persulphate.

In hot solutions containing excess of neutral sodium tartrate the dyes named are readily decolorized by titanium trichlorid.[1] The blue color readily returns in the case of the indigo carmine on shaking with air if the reducing agent has been added carefully, avoiding excess. With erythrosine and light green SF yellowish the color is scarcely restored at all by air, but on cooling and adding potassium persulphate it returns imperfectly. The reduction products of the other dyes do not give colored solutions again on oxidation, disregarding a slight yellowish or brownish tint that may sometimes appear.

Relatively few good tests are known for the common natural colors. Below are summarized some of the most useful analytical properties.[2]

In general these tests should be applied to the somewhat purified solutions of the coloring matter obtained by the use of solvents, as indicated on pages 75–78. Ether solutions may be evaporated to dryness, the residue warmed with a little alcohol and the alcoholic solution finally diluted somewhat with water.

By addition of concentrated hydrochloric acid the yellow ether or alcohol solution of carotin and xanthophyll show little change, becoming, perhaps, slightly paler. Green chlorophyll solutions become more brownish. Annatto in ether or alcoholic solutions remain orange, suffering little change. Turmeric solutions in ether or alcohol are characterized by their pure yellow color and slight green fluorescence, and on addition of several volumes of concentrated hydrochloric acid the color passes to orange red or carmine red. The orange or orange-yellow solutions of the redwoods, barwood, camwood, sandalwood, and Brazil wood, also of logwood, become deep red with excess of hydrochloric acid. The slightly colored neutral or faintly acid aqueous solutions of the flavone colors of fustic, Persian berries, quercitron, etc., become intensely yellow with 2 to 4 volumes concentrated acid. Neutral or slightly acid solutions of cochineal, archil, saffron, and caramel show little change.

Slightly acid solutions of various coloring matters show the behavior described below when treated with a little sodium hydroxid solution: Carotin and xanthophyll, little change; chlorophyll, "brown phase" reaction; alkanet, deep blue; turmeric, orange brown; the redwoods, violet red; logwood, violet to violet blue; the flavone colors become bright yellow; saffron remains yellow, showing little change. The red solutions of archil and the orange of cochineal become blue and violet, respectively. Caramel shows little change, becoming slightly deeper brown. The red fruit colors change to green, dull blue, or slate color, usually very quickly becoming browner by oxidation.

With sodium hydrosulphite in acid solution, the yellow coloring matters are little affected. Logwood is almost decolorized, the color returning inperfectly by reoxidation. Archil is decolorized, the color returning when shaken with air, but the reaction is more easily seen in alkaline solution. Cochineal shows no marked change. The anthocyanidins derived by hydrolysis from the red fruit colors are almost decolorized by hydrosulphite. Caramel is rendered slightly paler.

---

[1] Knocht and Hibbert. New Reduction Methods in Volumetric Analysis.

[2] For tables showing properties especially useful in analyses, see, especially, Berry, U. S. Bur. Chem. Circ. 25; Loomis, U. S. Bur. Chem. Circ. 63; Seeker, Allen's Commercial Organic Analysis, 4th ed., vol. 5; Leach, Food Inspection and Analysis. The properties of pure preparations of the various natural coloring matters, as described by the numerous investigators who have isolated and studied them, are described, for the most part, in H. Rupe's Chemie der Natürlichen Farbstoffe, Braunschweig, 1900 and 1909. Properties of the chlorophylls and carotinoids are given by Willstätter and Stoll, Untersuchungen über Chlorophyll, Berlin, 1913. Those of the coloring matters of the cornflower, rose, perlargona flower, larkspur, cranberry, whortleberry, and purple grape are described by Willstätter, Sitz. preuss. Akad. d. Wiss., 1914, **12**: 402.

Ferric chlorid gives no marked change with annatto or turmeric, or with saffron, these, perhaps, appearing somewhat browner. With the flavone colors, dark olive green to black colorations are produced. With the redwoods and logwood, very dark shades of violet, brown, or black are obtained (the first hue being often evanescent); cochineal becomes slightly darker; caramel is not affected. The solutions must be practically neutral.

Addition of alum solution renders the yellow color of logwood rose red (rather slowly). The redwoods behave similarly. The pale yellow solutions of the flavones become more strongly yellow, that of fustic, especially, developing a green fluorescence. Saffron and turmeric show little change.

Uranium acetate in neutral or nearly neutral solutions gives orange colorations with the flavones. Turmeric becomes somewhat browner; saffron is not affected. Cochineal becomes green;[1] alkanet, yellowish green; logwood, violet quickly fading.

The coloration with concentrated sulphuric acid dropped on the dry coloring matter for carotin and xanthyophyll is blue, usually obtained with difficulty. Annatto and saffron also give blue colors; turmeric a red; the flavone colors, yellow to orange colorations; alkanet and archil give violet blue; logwood, red changing to yellow.

Some special tests for natural coloring matters not indicated in the preceding statement are given below:

The "brown phase" reaction[2] may be useful for the characterization of chlorophyll, when this has not been previously treated with alkalies. The green ether or petroleum ether solution of the coloring matter, when treated with a little methyl alcohol solution of potassium hydroxid, becomes first brown, returning to green in a few minutes.

Leach's test[3] for annatto consists in pouring the alkaline solution of the color (obtained by shaking out the oil or melted and filtered fat with warm dilute sodium hydroxid solution) on a moistened filter. If annatto is present the filter proper will absorb the color so that when washed with a gentle stream of water it will remain dyed a straw color. If, after drying the filter, the color turns pink on application of a drop of stannous chlorid solution, the presence of annatto is confirmed.

The highly characteristic reaction of curcumine (turmeric) with boric acid may be conveniently carried out as follows: The aqueous or dilute alcoholic solution of the color is treated with hydrochloric acid until the shade just begins to appear slightly orange. The mixture is then divided in two parts and some boric-acid powder or crystals added to one. A marked reddening will be quickly apparent, best seen by comparison with the portion to which the boric acid has not been added. The test may also be made[4] by dipping a piece of filter paper in the alcoholic solution of the coloring matter, drying at 100°C., then moistening with a week solution of boric acid to which has been added a few drops of hydrochloric acid. On drying again a cherry red color will be developed.

---

[1] Girard and Dupré, Analyse des Matières Alimentaires.

[2] Molisch, Ber. botan. Ges., 1896, **14**: 16; Willstätter and Stoll, Untersuchungen über Chlorophyll, 144.

[3] Leach, Food Inspection and Analysis, 3d ed., p. 536. Here also are described the useful tests of Martin, Moore, Doolittle, and Cornelison for coloring matters in butter.

[4] Allen's Commercial Organic Analysis; U. S. Bur. Chem. Bul. 107.

SACCHARIN PRODUCTS.

It is recommended—

(1) That Fiehe's test, as modified by Bryan, as reported by the associate referee, be adopted as provisional.

(Adopted).

(2) That Feder's aniline chlorin test, as reported by the associate referee, be published with a view to adoption as provisional in 1916; except that the sentence "The intensity of the color is proportional to the amount present" be stricken out.

Approved.

FRUIT PRODUCTS.

It is recommended—

(1) That the Kunz modification of Stahre's method for the determination of citric acid be further studied.

Approved.

(2) That the uranyl-acetate and ammonium heptomolybdate methods for the determination of malic acid be further studied.

Approved.

(3) That the method for "Tartaric, citric, and malic acid (Schmidt-Hiepe method modified)" (U. S. Bur. Chem. Bul. 107 (rev.), pp. 80–81) be dropped.

Approved.

WINE.

It is recommended—

That the provisional method be dropped, and the method as reported by the associate referee be adopted for the determination of total tartaric acid in wines, grape juices, and soda-fountain sirups.

Approved.

BEER.

It is recommended—

That the methods for the determination of maltose and dextrin be made the subject of study for the coming year.

Approved.

FLAVORING EXTRACTS.

It is recommended—

(1) That the saponification method of Hortvet and West for methyl salicylate in wintergreen extract, approved by the association in 1914, be adopted as provisional.

Adopted.

(2) That the following method, devised by Hortvet and West, and described in the Journal of Industrial and Engineering Chemistry, volume 1, No. 1, be made provisional for anise and nutmeg extracts:

To 10 cc. extract in a Babcock milk flask add 1 cc. of hydrochloric acid (1: 1), then sufficient half-saturated salt solution previously heated to 60°C. to fill the flask nearly to the neck. Cork and let stand in water at 60°C. for about 15 minutes, occasionally giving the flask a twisting motion, and centrifuge for 10 minutes at about 800 revolutions per minute. Add brine till the oil rises into the neck of the bottle, and again centrifuge for 10 minutes. If the separation is not satisfactory, or the liquid is not clear, cool to about 10°C. and centrifuge for an additional 10 minutes. Multiply the reading by 2 to obtain the percentage of oil by volume.

Adopted.

(3) That the following slight modification of the Howard-Mitchell method, which has been studied during the last two years, be now provisionally adopted for peppermint and spearmint extracts, and for the determination of oil in wintergreen extract:

Pipette 10 cc. of the extract into a Babcock milk bottle, add 1 cc. of carbon disulphate, mix thoroughly, then add 35 cc. of cold water and 1 cc. concentrated hydrochloric acid. Close the mouth of the bottle with the thumb, and shake vigorously, whirl the bottle in a centrifuge for six minutes and remove all but 3 or 4 cc. of the supernatant liquid, which should be practically clear, by means of a glass tube of small bore, and aspiration. Connect the stem of the bottle with a filter pump, immerse the bottle in water kept at approximately 70°C. for three minutes, removing from the bath every 15 seconds and shaking vigorously. Continue in the same manner for 45 seconds, using a boiling water bath. Remove from the bath and shake while cooling. Disconnect from the suction and fill the bottle to the neck with saturated salt solution at room temperature, centrifuge for two minutes and read the volume of the separated oil from the top of the meniscus. Multiply the reading by 2 to obtain the percentage of oil by volume. In case of wintergreen, use as floating medium a mixture of 1 volume of concentrated sulphuric acid and 3 volumes of saturated sodium sulphate solution.

Adopted.

SPICES.

It is recommended—

(1) That the associate referee's modification of the distillation method for water in spices be given further study.

Approved.

(2) That the subject of ash determination in herbs be further studied, with particular reference to the influence of the exact temperature employed in the combustion.

Approved.

BAKING POWDERS.

It is recommended—

(1) That the Exner method for the gravimetric estimation of lead, as reported by the associate referee, be adopted as provisional.

Adopted.

(2) That the methods of Dunlap and Collins and the application of the Winkler method to the Remington modification of the colorimetric methods for the estimation of lead be further studied.

Adopted.

MEAT AND FISH.

It is recommended—

(1) That Price's method (U. S. Bur. Chem. Circ. 108, p. 10) be made a provisional method for starch in meat products in place of Mayrhofer's method (U. S. Bur. Chem. Bul. 107 (rev.), p. 109 (b)). With very little modification from Price's description, the official description should be:

In a 200 cc. beaker treat 10 grams of finely divided meat with 75 cc. of an 8% solution of potassium hydrate in 95% alcohol, and heat on the steam bath until all the meat is dissolved. This will require from 30 to 45 minutes. Add an equal volume of 95% alcohol, cool, and allow to stand at least one hour. Filter by suction through a thin layer of asbestos in a Gooch crucible. Wash twice with warm 4% potassium hydrate in 50% alcohol and then twice with warm 50% alcohol. Discard the washings. Endeavor to retain as much of the precipitate in the beaker as possible until the last washing. Place the crucible with contents in the original beaker, add 40 cc. of water and then 25 cc. of concentrated sulphuric acid. Stir during the addition of the acid and see that the acid comes in contact with all the precipitate. Allow to stand about 5 minutes, add 40 cc. of water, and heat just to boiling, stirring constantly. Transfer the solution to a 500 cc. graduated flask, add 2 cc. of a 20% aqueous solution of phospho-tungstic acid, allow to cool to room temperature, and make up to mark with distilled water. Filter through a starch-free filter paper, and determine the dextrose present in a 50 cc. portion of the filtrate with Fehling's solution after neutralizing the acid, using Low's method, as given in U. S. Bureau of Chemistry Bulletin 107 (revised), page 241, for the determination of the copper in the cuprous oxid precipitate, or the latter may be weighed as directed on page 242. The amount of dextrose multiplied by 0.9 gives the equivalent in starch.

Approved.

(2) That comparative studies be continued of the different determinations of the nitrogen distribution and the best manner of carrying them out as applied to extracts of fish flesh. Efforts should be made to standardize the method of determining coagulable proteins in such work. New methods proposed for the determination of proteoses, amino acids, amines, etc., in biological material should be investigated with a view to finding more sensitive and more accurate indices of deterioration in fish.

Approved.

(3) That a study be made of the value of volatile distillation products like amines, indol, etc., in detecting incipient decomposition in fish.

Approved.

FATS AND OILS.

It is recommended—

That special study be made of methods for the analysis of hydrogenated oils.

Approved.

DAIRY PRODUCTS.

It is recommended—

That the Roese-Gottleib method be adopted as official for the determination of fat in milk and condensed milk, both sweetened and unsweetened.

Adopted.

(2) That a further study be made of the Roese-Gottleib method in the analysis of ice cream, milk powders, malted milks, and milk chocolates.

Approved.

(3) That a special study be made of modifications of the Babcock method as applied to condensed milk, both sweetened and unsweetened, and to ice cream.

Approved.

(4) That the Babcock asbestos method (U. S. Bur. Chem. Bul. 107 (rev.), p. 119 (a)) and the paper coil method (ibid., p. 120 (b)) be dropped.

Approved.

CEREAL PRODUCTS.

It is recommended—

(1) That the following method for estimating the acidity of the water extract of flour be published with a view to its adoption as a provisional method in 1916:

Weigh out 18 grams of flour into a 500 cc. Erlenmeyer flask and add 200 cc. distilled water free from carbon dioxid. Place flask in water oven kept at a temperature of 40°C. for 2 hours, shaking vigorously every half hour; filter through dry double filters, rejecting the first 10 cc. of filtrate, until 100 cc. is obtained. Titrate with N/20 sodium hydroxid, using phenolphthalein as an indicator. Each cubic centimeter of sodium hydroxid solution represents 0.050% of acidity in lactic acid.

Approved.

(2) That the methods for gluten and moisture be made the subject of further study.

Approved.

TEA AND COFFEE.

It is recommended—

(1) That the Stahlschmidt method as reported by the associate referee for the determination of caffein in tea and coffee be published, with a view to its adoption as a provisional method in 1916.

Approved.

(2) That the method be further tried on a greater variety of teas and coffees, and it is suggested that the referee for next year study methods for determining tannin in tea and coffee.

Approved.

(3) That the Dvorkovitsch method (15) for caffein, under tea, and the Hilger and Fricke method (16) for caffein, under coffee, be dropped.

Approved.

PRESERVATIVES.

It is recommended—

(1) That the Fincke method adopted provisionally in 1914 be made official.

Read and placed on record for final action in 1916.

(2) That further study be made of the methods for the determination of saccharin, including the method proposed by Gnadinger.

Approved.

HEAVY METALS IN FOODS.

It is recommended—

(1) That coöperation with the associate referee on baking powder in the study of methods for the determination of lead in baking powder and baking-powder materials be continued.

Approved.

(2) That the gravimetric and volumetric methods for tin, tested this year, be adopted by the association as provisional.

Adopted.

(3) That further study be made of other methods for the determination of tin.

Approved.

(4) That the Gutzeit determination for arsenic be printed, with a view to its provisional adoption in 1916.

Approved.

(5) That study be made of the various modifications of the Gutzeit method for arsenic as applied to specific substances such as gelatin, following the procedure described in U. S. Bureau of Chemistry Circular 102.

Approved.

(6) That a study of some modification of the Marsh method for the determination of arsenic be made.

Approved.

(7) That the methods for the determination of copper, zinc, nickel, and aluminum in food products be made the subject of study by the association as soon as possible.

Approved.

(8) That the designation of this portion of the work be changed to "Metals in foods."

Approved.

REPORT OF COMMITTEE ON EDITING METHODS OF ANALYSIS.

By R. E. Doolittle (Food and Drug Inspection Laboratory, New York, N. Y.) *Chairman.*

Your committee on editing methods of analysis begs leave to report that it has completed the work assigned and herewith submits for your consideration the revised methods. The committee has included all authorized changes and additions, has eliminated obsolete methods in so far as possible, rewritten the text where parts appeared obscure, and made such consolidations of general methods and rearrangements as in its opinion would promote brevity and clearness.

In order that the members of the association may have an opportunity to criticize the revised methods, it is suggested by your committee that this report be published in the Journal of the association with view to final adoption of the methods in 1916.

Motion to the above effect made, seconded, and passed.

The meeting adjourned at 4.45 p.m. for the day.

THIRD DAY.

WEDNESDAY—MORNING SESSION.

REPORT ON PHOSPHORIC ACID.

By L. S. Walker (Agricultural Experiment Station, Amherst, Mass.), *Referee.*[1]

The work on phosphoric acid has been conducted along the same lines as last year with one or two exceptions. It was recommended that the standard solutions used in the optional volumetric method be standardized against a phosphatic material of known composition. The use of a synthetic solution was not made owing to lack of time and that last year the results showed very close agreements. Early in March samples and methods were sent to nineteen chemists who had previously signified their intention to coöperate in the work. Methods outlined were as follows:

INSTRUCTIONS TO COLLABORATORS.

Samples 1, 2, 3, and 4 are basic slags.

(A) Determine moisture in samples 1, 2, 3, and 4 at 100°C.

(B) Determine total phosphoric acid in samples 1, 2, 3, and 4 by each of the following methods:

(a) *Official gravimetric method,* using (a_7) method of making solution (U. S. Bur. Chem. Bul. 107 (rev.), p. 2).—Dehydrate an aliquot (20 cc.) of the basic slag solutions by evaporating to dryness on a steam or hot-water bath; take up with 5 cc. HCl and 25 cc. of hot water; digest to complete solution and filter off SiO_2. From this point proceed as directed for determination of total phosphoric acid (ibid., p. 3). *Before precipitating with magnesia mixture,* add 5 cc. of 5% sodium acetate.

(b) *Optional volumetric method.*—Determine phosphoric acid in an aliquot of solutions (a_7) by the optional volumetric method (b) (ibid. p. 4), standardizing the solutions against a standard phosphate material of approximately the same composition as the sample to be worked on.

(c) *Lorenz method* (Landw. Vers.-Sta. **55**: 183).—Dissolve 2 grams of basic slag in 15 cc. concentrated H_2SO_4 and 5 cc. concentrated HNO_3, cool and make up to 200 cc. Into a 200 to 250 cc. beaker measure carefully 20 cc. of the solution and add enough nitric acid (specific gravity 1.20) to bring the volume to 50 cc. The solution, without stirring rod, is then heated over a wire gauze until the first air bubbles appear. Take from the flame and rotate a few times so that the sides of the beaker will not be overheated and add at once, into the middle of the solution, 50 cc. of the sulpho-molybdate reagent. After the precipitate has settled to the bottom, 5 minutes at the longest, stir vigorously for one-half minute with a glass rod.

---

[1] Presented by H. D. Haskins.

Cover the beaker and allow to stand overnight. Filter through a platinum or porcelain Gooch crucible, using a single thickness of ash- and fat-free filter paper in the bottom. If the paper is cut so that it just fits the bottom of the crucible, without turning up on the sides, no trouble will be experienced with the precipitate running through. The precipitate should be washed four or five times with 2% ammonium nitrate solution and all the yellow precipitate carefully transferred to the crucible. The precipitate is then washed by filling the crucible once full and twice half full with alcohol 95% and allowing it to run dry after each addition. It is next washed with ether in the same manner. The crucibles containing the precipitates are placed in a fairly large desiccator (without H_2SO_4 or $CaCl_2$) exhausted to 100 to 200 mm. pressure, and allowed to remain one-half hour before weighing. The weight of ammonium-phosphomolybdate multiplied by the factor 0.03295 gives the amount of phosphoric acid (P_2O_5).

(NOTE.—The solution of basic slag prepared by the (a_7) method may be used, but in this case the aliquot portion must be made up to 50 cc. with the sulphuric-nitric acid mixture described for this method under available phosphoric acid.)

Preparation of reagents for Lorenz method—sulpho-molybdate solution.—In a 2-liter glass cylinder add 100 grams of pure dry ammonium sulphate and 1,000 cc. nitric acid (specific gravity 1.36) and stir until the sulphate is dissolved. In a 1,000 cc. flask dissolve 300 grams of pure dry ammonium molybdate in hot water, cool to about 20°C., fill to the mark, and pour in a thin stream into the nitric acid-ammonium sulphate solution. Allow to stand 48 hours at room temperature, filter through acid resistant paper, and preserve in a glass-stoppered bottle in a cool, dark place.

(C) Available phosphoric acid—preparation of solutions.

(1) *Concentrated solution of citric acid* (10%).—Dissolve in water exactly 200 grams of chemically pure crystallized citric acid having its full percentage of water of crystallization. Make up to exactly 2 liters. (Where a large number of analyses are to be made, one-half gram of salicylic acid should be added to the liter of this solution to prevent decomposition.)

(2) *Dilute solution of citric acid* (2%).—Mix exactly one volume of the concentrated citric-acid solution with four volumes of water. The resulting solution should have a temperature of about 17.50°C. when used.

(a) Making citric solution: Weigh 5 grams of the basic slag; transfer to a one-half liter Wagner flask containing 5 cc. of 95% alcohol. The flask should have a neck width of at least 20 mm. and be marked at least 8 cm. below the mouth. Make up to the mark with dilute citric-acid solution (2%) of a temperature of 17.5°C. Fit the flask with a rubber stopper and put at once into the rotary apparatus for 30 minutes, making 30 to 40 revolutions per minute. Take off and filter immediately through a folded S. & S. No. 597 filter paper.

(b) As soon as the filtration is completed, analyze according to the following methods:

(1) *Molybdate method* (provisionally adopted 1911).—To 50 cc. of the clear filtrate add 100 cc. of molybdate solution made according to the official methods. Put the beaker into a water bath until the temperature reaches 65°C., take out and allow to cool at ordinary temperature. Then filter, and wash the yellow precipitate of phosphomolybdate of ammonia four or five times with 1% nitric acid. Dissolve in 100 cc. of 2% ammonium hydroxid (cold), nearly neutralize with hydrochloric acid, and add to the solution 15 cc. of magnesia mixture (made according to the official method) drop by drop during continuous stirring. After 15 minutes add 10 to 12 cc. of ammonium hydroxid solution (specific gravity 0.90), then cover the

beaker with a glass cover and allow to stand for about two hours. Filter the double phosphate of ammonia and magnesia through a tared platinum Gooch crucible, wash six times with 2% ammonium hydroxid, dry, and proceed as customary for phosphoric acid determination.

(NOTE.—Better results will be obtained if a smaller aliquot is taken, and it is suggested that 20 to 25 cc. be used. *Before precipitating with magnesia mixture add 5 cc. of 5% sodium acetate solution.*

(2) *Optional volumetric method.*—Determine phosphoric acid in an aliquot of the clear solutions by the optional volumetric method (b) (U. S. Bur. Chem. Bul. 107 (rev.), p. 4).

(3) *Lorenz method.*—This method is conducted in exactly the same manner as for total phosphoric acid with one exception. The solution of basic slag (20 cc.) is made up to 50 cc. with the sulphuric-nitric acid mixture, prepared by mixing 30 cc. of sulphuric acid (specific gravity 1.84) to 1 liter of nitric acid (specific gravity 1.20).

(4) *Iron-citrate method* (Landw. Vers.-Sta., **79–80:** 260).—To 50 cc. of the citric acid solution of basic slag add in succession 25 cc. of the iron citrate solution, 10 cc. of 0.3% hydrogen peroxid, and 25 cc. of magnesia mixture. Put under stirring apparatus from 15 to 30 minutes, filter, ignite, and weigh. It is suggested that the solutions be put under the stirring apparatus before the magnesia mixture is added and that the magnesia mixture be added rather slowly.

Preparation of reagents for iron citrate method—iron citrate solution.—Place 1,000 grams of citric acid in a porcelain evaporating dish and pour over it a solution of iron chlorid containing 30 grams in 50 cc. water. Slowly and carefully add 4,000 cc. 20% ammonium hydroxid. After all has dissolved pour into 5,000 cc. flask and when cold fill to mark with water. Filter before using.

Magnesia mixture.—Dissolve 550 grams magnesium chlorid and 700 grams ammonium chlorid in a 10-liter flask with about 2,000 cc. of water. After the solution is complete add 1,750 cc. of 20% ammonium hydroxid and fill to mark with water. Filter after several days' standing.

PRECAUTIONS AND FURTHER INFORMATION.

(1) A photograph and detailed drawings of an inexpensive but efficient shaking apparatus were sent out by the referee for 1911. A copy of this will be forwarded to anyone coöperating in this work this year upon request to the referee.

(2) The rotary apparatus prescribed for shaking the flasks must not be substituted by ordinary shaking or rocker apparatus, as the latter differs in construction and effect. The rotary apparatus must turn round its axle 30 to 40 times per minute. Variations with these limits have no marked influence on the results.

(3) The half-liter flasks (after the design of Wagner) must have a neck width of at least 20 mm. and be marked at least 8 cm. below the mouth. These two points are important, for if the neck width is too narrow and the mark too high, the result will be too low, owing to the movement of the liquid being so limited. (The proper flasks are listed in E. & A. catalogue (1913), 3172.)

(4) The filtration must be done immediately after 30 minutes' rotation, and it is recommended to use the folded S. & S. No. 597 filter paper of such size that the whole quantity of the liquid can be poured onto the filter at once. Small and bad filtering papers give rise to error, in consequence of too slow filtration. If at first the filtrate is not clear, it must be again filtered (through the same filter) until it becomes clear.

(5) If the beaker containing the mixture of phosphatic and molybdenic solutions is put into the water bath until the temperature reaches between 60° and 70°C., a

Comparative work on basic slag.

ANALYST	MOISTURE	TOTAL PHOSPHORIC ACID			AVAILABLE PHOSPHORIC ACID			
		Official gravimetric method	Optional volumetric method	Lorenz method	Molybdate method	Optional volumetric method	Lorenz method	Iron-citrate method
SAMPLE 1.								
A. J. Patten, East Lansing, Mich.	0.23	[1]12.80	[1]13.01	[1]12.53	[1]12.50	[1]12.60	[1]12.25	[1]12.55
W. D. Richardson, Swift & Co., Chicago, Ill:								
Analyst A	0.11	[2]12.87	12.80	[1]13.18	[1]12.43	[1]12.43	[1]12.71	[1]11.88
Analyst B		[1]13.08	[3]12.93	[2]12.87	[1]12.42	[1]12.50	[1]12.82	[1]12.12
H. C. Moore and H. M. Hutson, Armour Fertilizer Works, Atlanta, Ga.	0.16	13.22	12.92	13.14	[4]11.98	12.18	12.40	12.58
L. S. Walker, Amherst, Mass.	0.25	[1]12.78	[1]13.00	[1]13.05	[1]12.51	[1]12.63	[1]12.12	[1]13.00
Average	0.19	12.95	12.93	12.95	12.47	12.47	12.46	12.43
SAMPLE 2.								
A. J. Patten, East Lansing, Mich.	0.30	18.35	[1]18.70	[1]18.00	[1]15.58	[1]15.28	[1]14.83	[1]14.95
W. D. Richardson, Swift & Co., Chicago, Ill.:								
Analyst A	0.24	[2]18.82	[2]17.94	[1]18.33	[1]15.23	[1]15.10	[1]15.42	[1]14.67
Analyst B		[1]18.82	[1]18.11	[2]17.99	[5]14.92	[1]15.18	[1]15.61	[1]14.86
H. C. Moore, H. M. Hutson, Armour Fertilizer Works, Atlanta, Ga.	0.28	18.60	17.82	18.34	[4]14.64	14.81	15.01	15.21
L. S. Walker, Amherst, Mass.	0.30	[1]18.45	[1]18.24	[1]18.21	[1]15.35	[1]15.20	[1]14.94	[1]15.10
Average	0.28	18.61	18.16	18.17	15.27	15.11	15.16	14.96
SAMPLE 3.								
A. J. Patten, East Lansing, Mich.	0.43	[1]15.20	[1]15.50	[1]14.78	[1]12.80	[1]12.78	[1]12.35	[1]12.50
W. D. Richardson, Swift & Co., Chicago, Ill.:								
Analyst A	0.27	[2]15.34	[2]14.82	[1]15.16	[1]13.39	[6]13.41	[1]13.69	[1]12.92
Analyst B		[1]15.23	[2]14.68	[5]14.97	[5]13.23	[6]13.40	[1]13.61	[1]13.14
H. C. Moore, H. M. Hutson, Armour Fertilizer Works, Atlanta, Ga.	0.36	15.41	14.75	14.91	12.88	13.07	13.37	13.39
L. S. Walker, Amherst, Mass.	0.29	[1]15.38	[1]15.32	[1]14.80	[1]13.06	[1]12.92	[1]13.10	[1]13.78
Average	0.34	15.31	15.01	14.92	13.07	12.92	13.22	13.15
SAMPLE 4.								
A. J. Patten, East Lansing, Mich.	0.30	[1]18.45	[1]18.45	[1]17.95	[1]14.45	[1]14.30	[1]13.95	[1]14.05
W. D. Richardson, Swift & Co., Chicago, Ill.:								
Analyst A	0.24	[5]18.65	[2]17.87	[1]18.36	[1]14.11	[1]14.14	[1]14.42	[1]13.47
Analyst B		[1]18.42	[5]18.08	[2]18.26	[5]14.04	[1]14.15	[1]14.46	13.65
H. C. Moore, H. M. Hutson, Armour Fertilizer Works, Atlanta, Ga.	0.29	18.84	17.91	18.40	[4]13.81	13.78	14.14	14.08
L. S. Walker, Amherst, Mass.	0.26	[1]18.50	[1]18.48	[1]18.63	[1]14.25	[1]14.18	[1]13.88	[1]14.22
Average	0.22	18.57	18.16	18.32	14.21	14.11	14.17	13.89

[1] Average of two determinations.
[2] Average of four determinations.
[3] Average of six determinations.
[4] Not included in average.
[5] Average of three determinations.
[6] Average of two determinations; not included in average.

precipitate free from silicic acid results. If heating is continued for a considerably longer time, the precipitate will often be mixed with silicic acid, especially when the molybdenic solution is not added to the filtrate immediately but only after 6 to 12 hours (or longer) after filtration. If silicic acid is present, the precipitate dissolves slowly in ammonia, but at first not clearly. Special attention must be paid to the point that the yellow precipitate is dissolved quickly and quite clearly by ammonia (2%), not made warm. If the solution becomes clear only after some time, molybdenic solution and nitric acid must be added to same in order to get a pure precipitate of phosphomolybdate of ammonia, or, in other words, the phosphoric acid must be reprecipitated by the molybdenic solution.

COMMENTS OF ANALYSTS.

A. J. Patten, East Lansing, Mich.: On total phosphoric acid the Lorenz method invariably gives results lower than the other two methods, while the official gravimetric and optional volumetric give results that agree fairly well with each other. For available phosphoric acid there is not so much difference in the results obtained by the four methods, although here also the molybdate and the optional volumetric agree with each other very well, and the Lorenz and iron citrate methods give results that agree with each other very well, but they are invariably a little lower than results by the other methods. It is my opinion that either the official gravimetric or optional volumetric, and possibly both, should be adopted by the association. If these methods are worked carefully and the necessary precautions are taken, I believe they give accurate results, and I can see no good reason for either the Lorenz or the iron citrate method.

DISCUSSION OF RESULTS.

The results this year are based upon the work of but five chemists. It was the idea of your referee to obtain results from as many collaborators as possible so that a large number of chemists would become more familiar with the methods.

In a study of the results by the different analysts the Lorenz method gave a lower figure than either the gravimetric or optional volumetric. This variation amounted in one case to over 1%. The iron-citrate method for available phosphoric also gave lower results than either the gravimetric or volumetric methods, except on sample No. 3. The greatest variation was over 1%. Both the iron citrate and Lorenz methods are easy of manipulation and somewhat shorter, but do not give as reliable results as the gravimetric and optional volumetric methods. Of these two latter methods, the gravimetric gave higher results in every case. The greatest difference for total phosphoric was 0.45% and for available phosphoric was 0.16%, the average being 0.24% and 0.10%, respectively. This would seem to indicate that silica has been thrown down with the

precipitate. It might be said here that this has been the experience of previous referees.

The writer realizes that it is impossible to recommend the adoption of any particular method for the analysis of basic slag until after the final report of the basic slag committee on field work has been submitted to the association. That is, each method should be checked up with the field results, and it seems advisable that the accumulation of analytical data be continued.

RECOMMENDATION.

It is recommended—

That further study of these methods be made with the idea of keeping them before the association until the field committee reports.

DISCUSSION RELATIVE TO REVISION OF METHODS.

Not long ago Dr. R. E. Doolittle, chairman of the committee on editing methods of analyses, called my attention to a few points which had come to his notice in revising the methods for phosphoric acid. Under the methods for the determination of phosphoric acid in basic slag, reference is made to the employment of the same method used for bones and tankages, based upon the fineness of the sample. U. S. Bureau of Chemistry Bulletin 107 (revised) does not, however, contain any such method.

The value of a basic slag cannot be determined by a mechanical analysis, because the nature of the product allows it to be adulterated with untreated phosphatic rock. In a paper read before the association in November, 1908, by H. D. Haskins, attention was called to this matter. Your referee believes that a method for the mechanical analysis of bones and tankages should be inserted in the official methods just before "(1) Preparation of sample." This would make "Preparation of sample" No. 2, "Moisture" No. 3, and "Phosphoric acid—official" No. 4. The writer would say, in this connection, that the method outlined under mechanical analysis is one which has been used in general for many years and has proved very satisfactory.

The methods as outlined in the official methods under (a) and (b), page 1, for preparing neutral ammonium citrate are obsolete and should be discontinued. The titration method, the litmus and azolitmin methods, are far more popular and efficient. The titration method as used in a great many laboratories gives excellent satisfaction, and is far superior to any other. Your referee believes that this method should be made official and published in the revision.

The provisional methods for the analysis of basic slag should be placed under (c) following "(5) Citrate-soluble phosphoric acid," on page 5.

SPECIFIC RECOMMENDATIONS.

It is recommended—

(1) That the following method for the mechanical analysis of bones and tankages be made official and inserted in official methods just above "(1) Preparation of sample:"

Transfer 10 grams or more of the original bone or tankage into a sieve having circular openings one-fiftieth of an inch in diameter. By means of a soft rubber pestle break all large lumps of the material which have a tendency to cake on standing. The part remaining in the sieve is weighed and called coarse. From this data the percentage of coarse and fine can be calculated.

(2) That the optional method for preparing neutral ammonium citrate solution under (a) and (b) be dropped and that the titration method which follows be made official:

Dissolve 370 grams of commercial citric acid in 1,500 cc. of water, add 358.33 cc. of ammonium hydroxid (specific gravity 0.90), and allow to cool. Fifty cubic centimeters of this citrate solution are carefully measured into a 250 cc. flask, made up to the mark with distilled water and thoroughly shaken. Five cubic centimeters of the diluted solution are then measured (preferably by means of a burette) into a beaker, 4 cc. of a perfectly neutral 40% solution of formaldehyde added, and titrated with N/10 NaOH, using phenolphthalein as an indicator. The pink color should remain after the solution is brought to boiling. The ammonia is determined in 5 cc. of the diluted solution in the usual manner by distilling with magnesia. The difference between the acid and ammonia titration gives the number of cubic centimeters of N/10 NH_3 required to neutralize 1 cc. of the citrate solution, from which the amount of a stronger solution of NH_4OH required to neutralize any given amount of the acid solution may be calculated.[1]

(3) That provisional methods on page 233 of Appendix be dropped.

(4) That the following methods be inserted after "(5) Citrate-soluble phosphoric acid" (p. 5):

(c) Thomas or Basic Slag—Provisional.

(1) preparation of sample.

Prepare the sample as directed for other fertilizers or fertilizing materials (p. 1).

(2) total phosphoric acid.

Make up the solution for the analysis as directed in a_7, page 2, under "(2) Total phosphoric acid," or in strong hydrochloric acid alone. In the latter case, after the portion for analysis is measured out, add nitric acid and heat for a few minutes.

(a) *Official gravimetric method.*—Dehydrate an aliquot (20 cc.) of the basic slag solutions by evaporating to dryness on a steam or hot water bath; take up with 5 cc. HCl and 25 cc. of hot water; digest to complete solution and filter off SiO_2. From this point proceed as directed for determination of total phosphoric acid (p. 3). *Before precipitating with magnesia mixture, add 5 cc. of 5% sodium acetate.*

---

[1] J. Ind. Eng. Chem., July, 1913, vol. 5, No. 7.

(b) *Optional volumetric method.*—Determine phosphoric acid in an aliquot of solutions (a_7) by the optional volumetric method (b) (p. 4), standardizing the solutions against a standard phosphate material of approximately the same composition as the sample to be worked on.

(3) CITRATE SOLUBLE PHOSPHORIC ACID (WAGNER'S METHOD).

(a) *The citric solution.*—Weigh 5 grams of the slag into a 500 cc. Wagner flask containing 5 cc. of 95% alcohol. (The flask should have a neck width of at least 22 mm. and should be marked at least 8 cm. below the mouth.) Make up to the mark with dilute citric-acid solution (2%) of a temperature of 17.5°C. Fit the flask with a rubber stopper and place at once in a rotary apparatus, shaking the flask for 30 minutes at the rate of 30 to 40 revolutions per minute, at the end of which time remove the flask and filter contents immediately.

(b) *Analysis of the citric solution.*—When the filtration is completed analyze the solution at once according to the following methods:

(c) *Molbydate method.*—To 50 cc. of the clear filtrate add 100 cc. of molybdate solution prepared according to the official method. Place the beaker containing this aliquot in a water bath, retaining it there until the temperature reaches 65°C., then remove from the bath and allow to cool to ordinary temperature. Then filter and wash the yellow precipitate of ammonium phosphomolybdate four or five times with 1% nitric acid. Dissolve the precipitate in 100 cc. of 2% cold ammonium hydroxid, nearly neutralize with hydrochloric acid, and add to the solution 15 cc. of the official magnesia mixture, drop by drop with continuous stirring. After 15 minutes add 10 to 12 cc. of ammonium hydroxid solution (specific gravity 0.90), cover the beaker with a watch glass, and allow to stand for about two hours. Filter the ammonium magnesium phosphate through a tared platinum Gooch crucible, wash six times with 2% ammonium hydroxid, dry, and proceed as in the usual phosphoric acid determination.

(d) *Optional volumetric method.*—Determine phosphoric acid in an aliquot of the clear solutions by the optional volumetric method (b) (p. 4).

REPORT ON USE OF CITRATES IN DETERMINATION OF PHOSPHORIC ACID.

W. J. JONES, JR. (Agricultural Experiment Station, Lafayette, Ind.), *Associate Referee.*

At the 1914 meeting of the association the question of whether neutral ammonium citrate, sodium citrate, or citric acid solution should be employed as a solvent in the determination of reverted phosphoric acid in fertilizers was referred to the associate referee.

Inasmuch as there is a considerable difference of opinion in the association regarding the proper method of preparing neutral ammonium citrate solution, it seemed to the associate referee that in order to secure results on which to base recommendations it was essential to investigate the various methods proposed for preparing the neutral ammonium citrate solution.

In taking up the investigation it was felt that the committee on recom-

mendations did not expect a complete report within one year, since the subject of substitutes for neutral ammonium citrate solution involves not only a large amount of analytical work but in addition a large amount of study, as the question of securing substitutes involves a review of the literature back at least to 1882, and possibly longer.

It being very evident that it is useless for the association to repeat work which has already been done and found wanting, before any profitable attempt to recommend substitutes can be made it is essential that all the reagents previously tried and the results of their use should be available.

In order to arrive at any conclusion in regard to substitutes, it is essential that promising reagents be used on a large number of samples, not only of raw materials but of fertilizers as they are prepared and offered for sale on the open markets.

It is essential before comparing the work of substitutes and citrate solutions that the various methods of preparing neutral ammonium citrate solution be carefully tested.

In investigating differences which have occurred between commercial chemists and the associate referee in official work, we have found that many of the differences charged to citrate solution were not due to difference in this reagent but to variations of the official method in preparing the samples for analysis, manipulation, etc. While the official method calls for analytical samples to be ground to pass a 1 mm. round-hole sieve, we have found in many cases that much finer grinding has been resorted to and the samples passed through a 20, 30, and 40 mesh sieve according to the views of the chemist making the determination.

In view of the preceding, in conjunction with Deputy State Chemist R. B. Deemer, and with the approval of the referee, we have taken up an investigation according to the following outline:

OUTLINE OF INVESTIGATION.

PREPARATION OF CITRATE SOLUTIONS.

(1) Present optional method with alcoholic calcium chlorid.
(2) Present official method, using saturated alcoholic solution of corallin.
(3) Patten's "titration method."
(4) Hildebrand's colorimetric method, using rosolic acid.
(5) Hall's conductivity method.
(6) Hand's purified litmus method, also azolitmin method as modified by U. S. Bureau of Chemistry Circular 52, and as modified by Rudnick.[1]
(7) Solution made with tri-ammonium citrate salt.

[1] J. Ind. Eng. Chem., vol. 5, No. 12.

(8) Solution made by neutralizing citric acid with ammonium hydroxid of known strength delivered underneath the citric acid solution.

SUBSTITUTES FOR NEUTRAL AMMONIUM CITRATE SOLUTIONS.

(9) Sodium citrate.
(10) N/10 citric acid solution.

OBJECTS SOUGHT IN INVESTIGATION.

(a) Effect of the use of these different solutions on the determination of reverted phosphoric acid by determining the amount of the same in a representative number of commercial fertilizers ground to pass a 100-mesh sieve by digestion with them in a mechanical agitator, thus removing any possible error due to difference in mechanical condition of the samples or manipulation.

(b) Investigation of the difference resulting in the amount of reverted phosphoric acid found due to grinding samples to different degrees of fineness by determining the amount of reverted phosphoric acid in above-mentioned samples ground to pass the 1 mm. round-hole sieve, 20, 40, and 100 mesh.

(c) Investigation of possible substitutes for neutral ammonium citrate, including sodium citrate solution as proposed by Bosworth, N/10 citric acid solution, and other citric acid solutions of various strengths, as well as other reagents which may give promise of proving satisfactory, and other points which may be developed as the work progresses.

PREPARATION OF ORGANIC MATERIAL FOR THE DETERMINATION OF PHOSPHORIC ACID AND POTASH IN ALIQUOTS OF THE SAME SOLUTION.

By R. M. West (Agricultural Experiment Station, St. Paul, Minn.).

The official methods of this association for the preparation of organic material in the determination of phosphoric acid[1] require a different procedure than for the preparation of the sample in the determination of potash.[2] The peculiar relationship which phosphorus and potassium bear to the fertility of a soil often makes it desirable to determine these two elements in the same plant material. Such was the case in our laboratory, and the following modification for the preparation of the sample was devised, which permits of the determination of phosphoric acid and potash in aliquot portions of the same solution. By following this method

[1] U. S. Bur. Chem. Bul. 107 (rev.), pp. 1–5.
[2] Ibid., pp. 11–12.

a marked saving of time can be effected when any considerable number of determinations are to be made.

PREPARATION OF SAMPLE.

Five grams of the finely ground sample are weighed out and transferred to a Kjeldahl digestion flask (Jena glass), 30 cc. of nitric acid (specific gravity 1.42) added, a small funnel placed in the mouth of the flask to serve as a condenser, and the mixture heated on a steam bath for about an hour. Ten cubic centimeters of hydrochloric acid (specific gravity 1.20) are then added and the digestion on the steam bath continued overnight. The following day, 20 cc. of sulphuric acid (specific gravity 1.84) are added, and the contents of the flask are boiled over a free flame. The flame should be so adjusted that when digestion is complete the volume of acid will be reduced to about 5 cc. The digestion is carried on in the same manner as a nitrogen digestion. The solution is then allowed to cool, transferred to a 250 cc. volumetric flask, made up to volume and aliquot portions are pipetted off for the determinations of potash and phosphoric acid according to the official methods of the association.

The method requires little or no attention from the analyst during the digestion, with the exception of the first few minutes following the addition of the sulphuric acid.

The preliminary treatment with aqua regia makes it possible to complete the subsequent digestion in a comparatively short time without the use of any other oxidizing agent, such as mercuric oxid, potassium sulphate, or copper sulphate.

The solution of the organic material with aqua regia alone, as preferred by the official volumetric method for phosphoric acid, in many cases was found to be unsatisfactory. This was particularly true when attempting the solution of material containing any appreciable amount of fat. The hot concentrated acid solution, even when apparently clear, gives a precipitate of organic matter when diluted with water in making up to volume. By the proposed method there is no difficulty in completely oxidizing all of the organic matter.

Evaporation of the sulphuric acid to about 5 cc. during digestion is advised, since a larger residue requires a correspondingly longer time for the evaporation to dryness of the portion measured out for the determination of potash.

The accompanying table shows the results of the analysis of various kinds of plant materials as prepared by the official method compared with those by the proposed method.

These results are fairly concordant and point clearly to the two following conclusions:

(1) The sulphuric acid digestion of organic matter does not interfere with the subsequent phosphoric acid determination.

Comparison of the results obtained in the determination of phosphoric acid and potash by the official and proposed methods for preparing the sample for analysis.

SAMPLE NO.	PHOSPHORIC ACID			POTASH		
	Proposed method	Official method	Difference	Proposed method	Official method	Difference
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	0.922	0.929	−0.007	0.16	0.16	0
2	0.976	0.985	−0.006	0.06	0.06	0
3	0.946	0.949	−0.003	1.35	1.37	−0.02
4	0.749	0.756	−0.007	2.11	2.09	+0.02
5	0.842	0.852	−0.010	0.63	0.67	−0.04
6	0.856	0.848	+0.008	1.21	1.25	−0.04
7	0.173	0.177	−0.004	1.40	1.39	+0.01
8	0.236	0.240	−0.004	1.34	1.35	−0.01
9	0.268	0.268	0.000	0.71	0.72	−0.01
10	0.574	0.577	−0.003	1.42	1.44	−0.02
11	0.657	0.655	+0.002	0.96	0.93	+0.03
12	0.639	0.642	−0.003	1.11	1.07	+0.04

(2) The use of Jena glassware for wet ignition of plant material with sulphuric acid does not affect the subsequent determination of potash.

These are the only two points on which the proposed method differs in principle from those approved by this association.

NEW METHOD FOR DRYING ETHER AND SAMPLE IN THE DETERMINATION OF ETHER EXTRACT.

By R. M. West (Agricultural Experiment Station, St. Paul, Minn.).

The official method of the association for the determination of crude fat, or ether extract, in foods and feeding stuffs[1] requires the use of anhydrous, alcohol-free ether with a moisture-free sample of the substance to be extracted.

Earlier investigators showed that this procedure was necessary, particularly for plant tissues, since the use of ordinary ether invariably yielded much larger quantities of ether extract, and the amount was apparently dependent largely upon the purity of the solvent used.

Wagner[2] compared the results obtained with absolute and ordinary ether on air dried and moisture free samples and found that where with ordinary ether and air dried material he obtained 13.00 per cent of extract, absolute ether dissolved only 10.54 per cent of the dried sample.

Atwater,[3] in his report of the committee on ways and means for securing more thorough chemical study of foods and feeding stuffs before this association in 1890, calls attention to the large extracts obtained with

[1] U. S. Bur. Chem. Bul. 107 (rev.), p. 39.

[2] Wagner, P. Fettbestimmung in Handelsfuttermitteln. Landw. Vers.-Sta., 1879, **24**: 289.

[3] U. S. Bur. Chem. Bul. 28, p. 120.

ordinary ether; and Schultze[1] et al., after a very exhaustive investigation, state, among other conclusions, that anhydrous ether must be used and that the material to be extracted must be carefully dried. Jones[2] in his report on feeds and feeding stuffs before this association, gave data leading to the same conclusions.

Methner,[3] on the other hand, in his investigations on the effect of the quality of ether on the results of fat determination in feeding stuffs, shows that small amounts of absolute alcohol added to absolute ether do not affect the amount of extract obtained.

It is to be concluded, therefore, that the high ether-extract values obtained with ordinary ether are due to the moisture content, and that, while anhydrous solvent and sample are necessary to a proper determination, the presence of small amounts of alcohol is not a source of error.

In spite of the requirements for dry solvent and sample in the official methods, many determinations of ether extract are made without drying either the sample or the ether. This practice is apparently becoming more and more common with the introduction of a number of "short methods."

These methods, as a rule, call for extraction with a comparatively large amount of solvent, which is then separated from the sample, made to volume, and the extract determined in an aliquot portion. The good agreement of results by this method with those by the official method has gained further popularity for them and has obscured what must be an example of two compensating errors, namely, an incomplete extraction on the one hand, being offset by the extraction of larger quantities of nonfatty material, soluble in the moist ether, on the other.

The time required in preparing the ether and the sample is a considerable item in such a procedure as the official method, where the time required for the extraction alone is 16 hours.

It appeared practical to shorten this by mixing a little powdered calcium carbid with the material to be extracted, thus drying it almost immediately and rendering the ether anhydrous at the time that it comes in contact with the sample.

The details of the method are as follows: Put about 2 grams of finely ground calcium carbid in the bottom of an extraction thimble, add the weighed sample (usually 2 grams) and then 5 or 6 grams more of the carbid. Mix the contents of the extraction thimble with a spatula and extract with ordinary ether in a Soxhlet extractor, completing the determination as prescribed by the official methods.

[1] Landw. Vers.-Sta., 1911, **75**: 185–230.
[2] J. Assoc. Off. Agr. Chem., 1913, **1**: 289–314.
[3] Chem. Ztg., 1899, **5**: (23) 37–38.

The use of the Soxhlet extractor is necessary as the generation of acetylene from the water in the ether during the first part of the extraction prevents the percolation of the ether through a continuous extraction tube of the Caldwell type.

A comparison of the results obtained by this method with those by the official method and those obtained with ordinary ether and air-dry sample are shown in the accompanying table. The results by the first two methods are in fairly close agreement, while with moist ether and sample they are in most cases materially higher. This is particularly true when samples of the whole plant have been extracted, and less marked for the cereal seeds, as in sample 5.

Comparison of results of the determination of ether extract.

NO.	MATERIAL	PROPOSED METHOD			OFFICIAL METHOD			ETHER AND SAMPLE NOT DRIED		
		1	2	Average	1	2	Average	1	2	Average
1	Alfalfa	1.76	1.70	1.73	1.68	1.67	1.68	2.81	2.53	2.67
2	Alfalfa	2.11	2.25	2.18	2.14	2.12	2.13	3.42	3.51	3.47
3	Alfalfa	1.87	1.92	1.90	1.90	1.96	1.93	3.18	3.26	3.22
4	Wheat	1.94	1.87	1.91	1.97	2.04	2.01	2.42	2.28	2.35
5	Wild rice seed	1.00	1.04	1.02	1.06	0.99	1.03	1.05	1.12	1.09
6	Wild rice stalk	0.94	0.80	0.87	0.94	0.94	0.94	2.45	2.23	2.34
7	Tomato plant	2.51	2.48	2.50	2.56	2.60	2.58	3.49	3.38	3.44
8	Sorghum cane	1.08	1.07	1.08	1.24	1.23	1.24	3.35	3.31	3.33
9	Wheat flour	0.76	0.80	0.78	0.81	0.79	0.80	1.00	1.05	1.03
10	Flax seed	35.52	35.60	35.56	35.81	35.90	35.86	36.69	36.65	36.67

There is no reason why a sample extracted by the proposed method is not equally available for a subsequent determination of crude fiber. It would be necessary, however, to use definite quantities of carbid and a correspondingly more concentrated acid for the acid digestion.

It seems probable that the use of calcium carbid and other dehydrating agents can be extended for this purpose to semifluids, animal tissues, and other substances, such as soaps and samples high in sugars, where difficulty is ordinarily experienced in obtaining a sample in the proper condition for fat extraction. The subject will be studied further in this connection.

The results show conclusively, however—

(1) That the use of ordinary ether and air-dry sample gives high results as compared with the official method.

(2) That the admixture of calcium carbid to the sample to be extracted is an effective and quiet method of drying both sample and solvent.

REPORT OF THE COMMITTEE ON AVAILABILITY OF PHOSPHORIC ACID IN BASIC SLAG.

At a meeting of your committee it was thought best to give the association a brief outline of the work undertaken and accomplished by the various experiment stations coöperating in the basic-slag investigations. The committee begs, therefore, to submit the following report:

The Rhode Island station last year made a report on the growth of millet and rape in pot-culture work. This year it has submitted the results of field investigations with both millet and rape. The field tests are to be continued another year to study the after effects of the different phosphatic materials.

The report from the Massachusetts station is incomplete for both field and pot work, due to an inability to deplete the soil of phosphoric acid sufficiently to start the experiments. One series of the pot work upon which rape was grown during the past year was, on the whole, unsatisfactory, on account of the large growth in the pots to which no phosphoric acid was added. It is believed, however, that valuable data has been secured even under these conditions, when studied from the standpoint of phosphoric acid recovered by crops from the various phosphatic materials applied. This station plans to continue the experiments another year, using a soil which is known to be deficient in phosphoric acid. Arrangements also have been made to carry on the final test in the field during the coming season which, during the past three years, has received the preliminary treatment necessary for the depletion of the soil in phosphoric acid.

In 1914 a report was made by the Hawaiian station. The work has been continued to study the after effects of the different phosphatic materials, but to date no further report has been made to the committee. It is understood that a report on this work has recently been prepared and submitted to the United States Department of Agriculture for publication.

A partial report on pot experiments was made in 1914 by the Texas station, on results secured with corn grown on five different types of soil. This work has been supplemented in 1915 by other results with sorghum and rye, using two additional types of soil over what was used during the previous year.

A report was made by the New Jersey station in 1913 on pot-culture work with buckwheat. In 1915 results with barley, buckwheat, and soy beans were submitted in which these crops were grown on an artificial soil composed of a white quartz sand.

A partial report has been made by the North Dakota station in which millet and rape were used as the crops in pot-culture work. From subsequent correspondence, it would appear doubtful whether further coöper-

ation may be expected from this institution. It is hoped, however, that other additional data asked for by the committee may be supplied later, particularly that with reference to the dry matter and phosphoric acid determinations on the crops grown.

Results of pot-culture experiments in 1913 with rape and in 1914 with wheat have been received from the Cornell station. In this case, as with the previous one, it seems highly important that the crops from each treatment be analyzed for their total content of phosphoric acid.

Reports from field experiments at the Pennsylvania station were made on results secured in 1914 with rape and in 1915 with wheat. It seems unfortunate to your committee that determinations of dry matter and total phosphoric acid were not included in the report.

In addition to the above, the field and pot work has been carried on by the Illinois, North Carolina, and Virginia stations, but to date only preliminary reports on the progress of the work have been made. The Louisiana and Delaware stations have not yet started the experiments, but have assured the committee they will do so as soon as practicable.

It would seem to the committee that other stations who are contemplating starting the work should strain a point to do so during the coming year, if possible.

The committee has experienced considerable difficulty in interpreting the results sent in from the various stations, as in many cases they have not been reported in sufficient detail, in accordance with the plan originally outlined by the committee.

In view of these facts, it has been thought best to prepare blanks or, standard forms, which will be furnished by the committee to each institution coöperating in the work.

C. B. Williams,
H. D. Haskins,
B. L. Hartwell,
C. G. Hopkins,
J. A. Bizzell,
Basic Slag Committee.

REPORT ON AVAILABILITY OF POTASH.

By E. E. Vanatta (Agricultural Experiment Station, Columbia, Mo.),
Referee.

The work reported this year is a continuation of that reported last year. The pot experiments have been conducted by J. T. Barlow, under the direction of M. F. Miller, of the soils department of the University of Missouri.

Seven series of pot cultures were run in duplicate. Series Nos. 2 to 6 were filled with a mixture of washed quartz sand, sufficient fine ground feldspar to supply 0.66% total potash (K_2O) to the mixture, and fertilizer to furnish sufficient N, P, Ca, Mg, Fe, and S for maximum plant growth.

Feldspar alone was added to series No. 1. Fertilizer, except feldspar or potash, was added to series No. 7.

In addition, the following treatments were given series Nos. 2 to 6:

Series No. 2.—Blue grass was added at the rate of 30,000 pounds per acre.

Series No. 3.—The feldspar was heated to 100°C.

Series No. 4.—Calcium carbonate was added at the rate of 4,500 pounds per acre.

Series No. 5.—Calcium oxid was added at the rate of 3,000 pounds per acre.

Series No. 6.—Starch was added at the rate of 10,000 pounds per acre.

Sweet corn was planted in the pots September 14, 1914. The crop was grown in the greenhouse and harvested December 12, 1916.

Dry weight of plants grown, in grams.

	Grams
Series No. 1 (sand and feldspar)	5.8
	7.4
Average	6.6
Series No. 2 (sand, feldspar, fertilizer, and blue grass)	13.04
	16.00
Average	14.70
Series No. 3 (sand, feldspar heated, and fertilizer)	7.6
	7.8
Average	7.7
Series No. 4 (sand, feldspar, fertilizer, and $CaCO_3$)	6.6
	5.8
Average	6.2
Series No. 5 (sand, feldspar, fertilizer, and CaO)	1.8
	3.2
Average	2.5
Series No. 6 (sand, feldspar, fertilizer, and starch)	1.1
	1.1
Average	1.1
Series No. 7 (sand and fertilizer)	9.3
	5.6
Average	7.5

The addition of a large amount of organic matter in the form of blue grass has evidently had a beneficial effect on plant growth, either by furnishing available potash on its decay or by liberating potash from the feldspar.

The addition of organic matter in the form of starch has retarded plant growth.

Calcium carbonate apparently has had slight effect on plant growth, while calcium oxid apparently has retarded plant growth.

The results of this work indicate that the potash compounds in feldspathic rock are of little value in furnishing readily available plant food.

REPORT ON DETERMINATION OF POTASH.

By T. D. Jarrell (Maryland Agricultural College, College Park, Md.), *Associate Referee.*

The coöperative work undertaken this year on the determination of potash has been along the lines recommended by the association at its last meeting, and has comprised—

(1) The perchlorate method.

(2) The use of denatured alcohol (U. S. Internal Revenue Formula 1) for washing K_2PtCl_6

(3) The necessity for the addition of hydrochloric acid to the water extract.

Before sending out instructions some preliminary work was carried on by E. E. Vanatta, referee on potash, and the associate referee, with the idea of improving upon the perchlorate method sent out last year.

Twenty chemists requested samples for coöperative work, but reports were received from only nine. A number of chemists who were desirous of participating in the work on the perchlorate method were prevented by being unable to secure perchloric acid.

The following directions were sent to coöperating chemists:

INSTRUCTIONS TO COLLABORATORS.

Sample No. 1.—Kainit.

Sample No. 2.—Mixture of acid phosphate, kainit, and muriate of potash (contains about 5% K_2O).

Sample No. 3.—Mixture of acid phosphate, sulphate of potash, and dried blood (contains about 8% K_2O).

Sample No. 1.

Determine potash by—

(*a*) *Official method.*—Weigh out 2.50 grams for a 250 cc. flask or 5 grams for a 500 cc. flask, and take 50 cc. aliquot for each determination corresponding to 0.50 gram charge.

(*b*) *Perchlorate method.*—Dissolve the potash as per the official method. While hot, precipitate the sulphates by adding drop by drop normal barium chlorid solution acidified with hydrochloric acid. Cool, make to mark, and shake. Filter, and transfer 50 cc. of the solution to an evaporating dish (glass dish is preferable), add 5 cc. of perchloric acid (specific gravity 1.12), evaporate on steam or sand bath until it fumes strongly, take up the residue with 10 cc. water, add a second 5 cc. of perchloric acid, and again evaporate the solution until all free hydrochloric acid is driven off and dense white fumes of perchloric acid appear. (If water bath is used for evaporation, place dish on hot plate and heat carefully until all free HCl is driven off.) After cooling add 20 cc. of 95% alcohol, stirring the precipitate well with the alcohol. After standing for one-half hour decant the alcohol through a prepared Gooch crucible, thoroughly draining. Transfer the precipitate to the crucible with 95% alcohol saturated at working temperature with pure potassium perchlorate. (See note 4 at end of instructions.) Thoroughly wash with about 125 cc. of the saturated alcohol, dry to constant weight at 120° C., and weigh. Wash again with another 50 cc. of saturated alcohol. If the loss in weight exceeds 0.0005 gram, rewash the precipitate until constant weight is obtained. After weighing, dissolve the precipitate from the crucible with hot water, dry, and weigh. If an insoluble residue is present, make corrections for same.

Samples Nos. 2 and 3.

Determine potash by—

(*a*) *Official method,* using the method for preparing the water extract as adopted officially in 1912 (U. S. Bur. Chem. Bul. 152, p. 41), which is as follows: Weigh 2.5 grams of the sample upon a 12.5 cm. filter paper and wash with successive small portions of boiling water into a 250 cc. graduated flask to a volume of about 200 cc. Add 2 cc. of concentrated HCl, heat to boiling, and add to the hot solution a slight excess of NH_4OH and sufficient ammonium oxalate to precipitate all lime present. Cool, dilute to 250 cc., mix, and filter. Use 50 cc. corresponding to 0.50 gram and proceed as in Bureau of Chemistry Bulletin 107, page 11.

(*b*) *Modified official method.*—This is same as the official method, except omitting the addition of 2 cc. concentrated HCl to water extract and boiling. After washing 2.5 grams on filter paper, add directly NH_4OH and ammonium oxalate, and proceed as per official method.

(*c*) *Official method, using denatured alcohol.*—Same as the official method (*a*), except use denatured alcohol for washing K_2PtCl_6 according to formula 1, United States Internal Revenue Regulations No. 30, revised August 22, 1911, page 45 (100 parts by volume of ethyl alcohol, 10 parts by volume of wood alcohol, and one-half of one part by volume of benzine). Add sufficient water to make 80% alcohol by volume.

(*d*) *Perchlorate method* (*$BaCl_2$ process*).—Proceed as per official method (*a*) until after the addition of 1 cc. of 1-to-1 H_2SO_4 and ignition. Dissolve residue in about 20 cc. hot water, add several drops of HCl, add normal barium chlorid solution slightly acidified with HCl in slight excess, filter into evaporating dish, wash the precipitate and filter paper with hot water, add 5 cc. perchloric acid to filtrate, evaporate on steam or sand bath until it fumes strongly, take up with a second 5 cc. of perchloric acid, and again evaporate until all free HCl is given off and dense white fumes of perchloric acid appear. (If water bath is used for evaporation, place the dish on hot plate and heat carefully until all free HCl is driven off.) Cool, add 20 cc. 95% alcohol, allow to stand one-half hour, filter, wash, dry, and weigh as described for sample No. 1.

(*e*) *Perchlorate method* (*$Ba(OH)_2$ process, Davis modification*).—Transfer 50 cc. of potash extract taken from same flasks as prepared for method above to a porcelain or silica dish (do not use platinum), add 15 cc. of 3% solution of barium hydroxid, and without filtering evaporate to dryness on steam bath. Gently ignite the residue over Bunsen burner below a red heat for 15 minutes. Extract the residue with boiling water, breaking up the material as much as possible, filter into an evaporating dish of about 175 cc. capacity (glass dish preferable), and wash with boiling water until the filtrate amounts to about 150 cc. Add perchloric acid and proceed as outlined in method (*d*) above. After weighing the $KClO_4$, wash it out with hot water in each perchlorate method, weigh again, and make corrections for any insoluble matter that may be present. Report whether you obtain any insoluble matter or not.

It is requested that you test thoroughly the modified official method; that is, omitting the addition of 2 cc. concentrated HCl to the potash extract, on some of your samples containing acid phosphate. If the addition of HCl gives higher results than omitting it, please report your reason for it. Report as fully on this phase as possible.

Also test thoroughly the use of denatured alcohol for washing K_2PtCl_6 made up as already described. This will probably be made an alternate official method for washing K_2PtCl_6 at the next meeting, since it was recommended at the last meeting of the association to be further studied this year with a view of its adoption officially in 1916. The benzine used for this formula must be a hydrocarbon product derived either from petroleum or coal tar. If benzine is used derived from petroleum, it may become somewhat cloudy on adding water, due probably to the partial separation of the petroleum product. Should this occur, it will not make any difference when used as a wash for K_2PtCl_6. If a cloudiness does occur report it, and also report which hydrocarbon product you use for preparing the denatured alcohol.

Precautions and Further Information.

(1) Factor for converting $KClO_4$ to K_2O, 0.34. Factor for converting K_2PtCl_6 to K_2O, 0.1938.

(2) The perchloric acid usually available has a specific gravity of 1.12 and contains about 20% acid. Should you use, however, weaker acid, it will, of course, be necessary to add corresponding larger amounts for each determination than directed. If a large excess of barium is added it may be necessary to add more perchloric acid than directed in order to change all barium to barium perchlorate. It is necessary to add sufficient $HClO_4$ to combine not only with the potash but with all other bases present in the solution. If this precaution is not observed high results will be obtained.

(3) Much of the perchloric acid now on the market contains a trace of potassium salts. In view of this fact, it will be necessary to make a blank determination for $KClO_4$ on the same amount of $HClO_4$ used for each determination, and deduct the quantity of $KClO_4$ it yields from the actual weight of $KClO_4$ obtained in the analysis. The blank determination should be carried on as follows: Evaporate 10 cc. of $HClO_4$, or the equivalent amount used for each determination, to dryness and take up with 95% alcohol. Filter the insoluble residue in a Gooch crucible, wash with 95% alcohol saturated with $KClO_4$, dry, and weigh. Please report the amount of $KClO_4$ found in 10 cc., $HClO_4$.

(4) In order to wash the final precipitate to constant weight it will be necessary to have the alcohol completely saturated at working temperature with $KClO_4$. It is difficult to obtain complete saturation unless the following precautions are

observed: The 95% alcohol must be shaken frequently with the pure, finely divided $KClO_4$ during at least 36 to 48 hours. It is necessary to filter off the "washing alcohol" immediately before use, so as to have the alcohol saturated at the actual temperature of working. The test for the satisfactory saturation of alcohol is that when 100 cc. of it is used to wash a precipitate of pure $KClO_4$ the loss in weight is not more than 0.0001 gram. It is convenient to keep a 2-liter flask full of alcohol, to which about 3 or 4 grams of pure $KClO_4$ is added.

(5) Take aliquots from same flasks for the different methods as far as possible. It is requested that you weigh out two or more charges for samples Nos. 2 and 3 and take duplicates from each flask for each method. This process will give a better comparison of methods than weighing out separate charges for each method.

(6) Report fully your opinion of the perchlorate method in comparison with the official Lindo-Gladding method, noting especially its accuracy, rapidity, and cheapness, if any, over the latter method (official). Also report your preference of the two perchlorate methods outlined for samples Nos. 2 and 3.

(7) Please report results not later than October 1.

RESULTS OBTAINED BY COLLABORATORS.

TABLE 1.

Comparison of methods for potash determinations (samples Nos. 1 and 2).

ANALYST	SAMPLE NO. 1		SAMPLE NO. 2				
	Method		Method				
	(*a*) Official	(*b*) Perchlorate	(*a*) Official	(*b*) Modified official (no HCL)	(*c*) Official using denatured alcohol	Perchlorate	
						$BaCl_2$ process	$Ba(OH)_2$ process
T. D. Jarrell, College Park, Md.	12.20	12.51	5.05	5.10	5.08	5.21	5.15
	12.42	12.42	5.09	5.09	5.08	5.10	5.24
	12.72	12.48	5.07	5.08	5.16	5.05	5.13
	12.52	12.72	5.05	5.09	5.15	5.17	5.02
	.....	12.72	5.10	5.07	5.05	5.13	.....
	.....	.....	5.09	5.06	5.12	5.13	.....
	.....	.....	5.06	5.05	5.05	.....	.....
	.....	.....	5.09	5.05	5.03	.....	.....
Average	12.41	12.57	5.08	5.07	5.09	5.13	5.14
E. G. Proulx, Lafayette, Ind.	12.32	12.61	5.08	4.96	5.04	5.34	5.24
	12.18	12.82	5.10	4.96	5.20	5.20	5.03
	12.14	13.11	5.08	4.86	5.22	5.26	5.23
	12.32	.....	.....	4.94	.....	5.22	5.25
	12.36	.....	.....	.....	.....	.....	5.22
Average	12.26	12.85	5.09	4.93	5.15	5.26	5.20
A. Wiberg, Pullman, Wash	11.95	12.26	5.13	4.95	5.05	5.39	5.35
	11.96	12.21	5.15	5.06	5.13	5.30	5.30
	.....	.....	5.15	5.00	5.06	5.31	5.30
	.....	.....	5.04	4.97	5.10	.....	.....
	.....	.....	5.13	5.08	.....	.....	.....
Average	11.96	12.24	5.12	5.01	5.09	5.33	5.32

TABLE 1—Continued.

ANALYST	SAMPLE NO. 1		SAMPLE NO. 2				
	Method		Method				
	(a)	(b)	(a)	(b)	(c)	Perchlorate	
	Official	Perchlorate	Official	Modified official (no HCl)	Official using denatured alcohol	$BaCl_2$ process	$Ba(OH)_2$ process
R. C. Wiley, Manhattan, Kans.	12.06	12.11	5.20	5.20	5.12	5.04	5.04
	12.02	12.18	5.08	5.20	5.20	5.10	5.10
	12.22	12.00	5.08	5.24	5.28	.....	5.11
	12.06	12.02	5.08	.....	.....	.....	.....
	.....	.....	5.16	.....	.....	.....	.....
Average	12.09	12.08	5.12	5.21	5.20	5.07	5.08
P. L. Hibbard, Berkeley, Cal.	12.00	12.76	5.06	5.05	5.10	5.16	[1]4.35
	11.96	12.10	5.02	5.07	5.02	5.10	4.80
	12.04	12.28	5.12	5.05	5.16	.....	4.94
	11.81	[1]13.02	5.12	5.26	5.06	.....	4.92
	.....	.....	.....	5.03	5.02	.....	.....
	.....	.....	.....	5.09	5.16	.....	.....
	.....	.....	.....	5.03	5.22	.....	.....
Average	11.95	12.38	5.08	5.08	5.11	5.13	4.89
F. B. Carpenter, Richmond, Va.	12.12	.....	4.94	.....	5.00	.....	.....
	12.20	.....	4.98	.....	4.92	.....	.....
	.....	.....	4.92	.....	.....	.....	.....
Average	12.16	.....	4.95	.....	4.96	.....	.....
W. D. Richardson, Chicago, Ill.	12.21	12.41	5.14	5.18	5.06	.....	.....
	12.23	12.38	5.18	5.08	5.08	.....	.....
	12.17	12.60	5.16	5.00	4.98	.....	.....
	12.12	12.34	.....	.....	5.04	.....	.....
Average	12.18	12.43	5.16	5.09	5.04	.....	.....
W. A. Davis, England	.....	12.14	.....	.....	.....	4.87	5.10
	.....	12.10	.....	.....	.....	4.91	4.97
	.....	12.27	.....	.....	.....	4.96	.....
Average	.....	12.17	.....	.....	.....	4.91	5.04
E. E. Vanatta, Columbia, Mo.[2]	11.81	11.93	4.97	5.08	4.87	5.47	4.84
General average	12.10	12.33	5.07	5.07	5.06	5.19	5.07

[1] Omitted from average.
Only average of results reported.

TABLE 2.

Comparison of methods for potash determinations (sample No. 3).

ANALYST	METHOD				
	(a) Official	(b) Modified official (no HCl)	(c) Official using denatured alcohol	Perchlorate	
				$BaCl_2$ process	$Ba(OH)_2$ process
T. D. Jarrell, College Park, Md.	8.63	8.58	8.53	8.63	8.31
	8.59	8.71	8.51	8.57	8.62
	8.50	8.65	8.79	8.83	8.43
	8.52	8.66	8.59	8.89	8.43
	8.58	8.63	8.78	.....	.....
	8.57	8.60	8.78	.....	.....
	.....	.....	8.55	.....	.....
	.....	.....	8.63	.....	.....
Average	8.57	8.64	8.65	8.73	8.45
E. G. Proulx, Lafayette, Ind.	8.52	8.68	8.56	8.92	8.03
	8.66	8.74	8.70	8.91	8.12
	8.56	8.66	8.68	8.83	8.21
	8.54	8.70	.....	8.84	8.21
	.....	.....	.....	8.89	8.08
	.....	.....	.....	8.91	.....
	.....	.....	.....	8.81	.....
Average	8.57	8.70	8.65	8.87	8.13
A. Wiberg, Pullman, Wash.	8.56	8.61	8.57	8.81	8.82
	8.64	8.57	8.55	8.79	8.82
	8.58	8.47	8.57	8.82	8.80
	8.62	8.48	8.56	8.82	8.81
	8.65	8.63	8.63	.....	.....
	8.60	8.62	.....	.....	.....
Average	8.61	8.56	8.58	8.81	8.81
R. C. Wiley, Manhattan, Kans.	8.54	8.54	8.57	8.48	8.38
	8.54	8.52	8.57	8.50	8.16
	8.54	.....	.....	.....	8.68
	8.52	.....	.....	.....	.....
Average	8.54	8.53	8.57	8.49	8.41
P. L. Hibbard, Berkeley, Cal.	8.62	8.46	8.58	8.78	8.52
	8.58	8.54	8.58	8.66	[1]9.04
	8.66	8.42	8.45	.....	8.35
	8.66	8.52	8.60	.....	8.87
	.....	8.58	8.46	.....	.....
	.....	.....	8.58	.....	.....
Average	8.63	8.50	8.50	8.72	8.58
F. B. Carpenter, Richmond, Va.	8.42	.....	8.30	.....	.....
	8.32	.....	8.28	.....	.....
	8.44	.....	.....	.....	.....
	8.42	.....	.....	.....	.....
Average	8.40	.....	8.29	.....	.....

[1] Omitted from average.

TABLE 2—Continued.

ANALYST	METHOD				
	(a) Official	(b) Modified official (no HCl)	(c) Official using denatured alcohol	Perchlorate	
				$BaCl_2$ process	$Ba(OH)_2$ process
W. D. Richardson, Chicago, Ill.	8.45	8.57	8.41	.....	.....
	8.59	8.59	8.60	.....	.....
	8.56	8.68	8.49	.....	.....
	8.62	8.66	8.52	.....	.....
Average	8.56	8.63	8.51	.....	.....
W. A. Davis, England	.....	.....	.....	8.40	8.44
	.....	.....	.....	8.50	8.34
	.....	.....	.....	8.33	.....
Average	.....	.....	.....	8.48	8.39
E. E. Vanatta, Columbia, Mo.[1]	8.49	8.49	8.46	8.51	8.66
General average	8.55	8.58	8.53	8.66	8.49

[1] Only average of results reported.]

Mr. Davis of the Rothamsted Experiment Station, England, reported the following figures showing a comparison of results on samples Nos. 2 and 3 by adding HCl to the water extract and by omitting it. He used the perchlorate method.

TABLE 3.

Comparison of methods for potash determinations (samples Nos. 2 and 3).

SAMPLE NO. 2				SAMPLE NO. 3			
Official method of preparing solution (with HCl)		Modified method of preparing solution (no HCl)		Official method of preparing solution (with HCl)		Modified method of preparing solution (no HCl)	
$BaCl_2$ process	$Ba(OH)_2$ process	$BaCl_2$ process	$Ba(OH)_2$ process	$BaCl_2$ process	$Ba(OH)_2$ process	$BaCl_2$ process	$Ba(OH)_2$ process
4.91	5.12	5.15	5.09	8.31	8.34	8.32	8.20
4.82	5.09	5.14	5.20	8.35	8.53	8.45	8.25
4.88	5.01	4.91	4.82	8.53	8.34	8.42	8.25
4.95	4.94	5.07	4.84	8.56	8.33	.....	8.53
4.86	.....	4.94	4.87	8.44	.....	.....	8.45
4.92	.....	.....	5.13	8.48	.....	.....	8.42
4.98	.....	.....	5.01	8.59	.....	.....	8.48
4.94	.....	.....	.....	.....	.....	.....	8.26
.....	.....	.....	.....	.....	.....	.....	8.30
[1]4.91	[1]5.04	[1]5.04	[1]4.99	[1]8.47	[1]8.39	[1]8.40	[1]8.35

[1] Average.

Mr. Davis also reported results on two samples prepared himself showing comparison of official method of preparing solution and modified official method (no HCl). He also used the perchlorate method in this work.

TABLE 4.

Comparison of results on the use of hydrochloric acid in potash determinations with different mixtures.

MIXTURE OF 1.25 GRAMS KAINIT AND 1.25 GRAMS ACID PHOSPHATE		MIXTURE OF 4 GRAMS KAINIT AND 2 GRAMS ACID PHOSPHATE	
With HCl	Without HCl	With HCl	Without HCl
6.69	6.54	8.09	8.22
6.47	6.68	8.07	8.26
6.66	6.64	8.10	8.29
.....	.....	8.20	.....
[1]6.61	[1]6.62	[1]8.12	[1]8.26

[1] Average.

Mr. P. L. Hibbard reported the following results on the use of HCl to the water extract. Three operators used the same mixtures, apparatus, and chemicals, but otherwise worked independently.

TABLE 5.

Comparison of results on the use of hydrochloric acid in potash determinations with different mixtures.

	ANALYST 1	ANALYST 2	ANALYST 3
NO. 1 MIXTURE.[1]			
With HCl.....	4.67	4.59	4.62
	4.77	4.60	4.68
	4.57	4.60	4.73
	4.72	4.60	4.70
Average[2].....	4.68	4.60	4.68
Without HCl.....	4.64	4.55	4.71
	4.62	4.59	4.72
	4.69	4.56	4.69
	4.66	4.60	4.72
Average[3].....	4.65	4.57	4.71
NO. 2 MIXTURE.[4]			
With HCl.....	8.77	9.08	9.12
	8.85	9.07	9.00
	9.12	9.07	9.25
	9.10	9.07	9.06
Average[5].....	8.96	9.07	9.11
Without HCl.....	9.06	9.06	8.70
	9.17	8.97	8.79
	9.20	9.06	9.04
	9.17	9.05	9.15
Average[6].....	9.15	9.04	8.92

[1] Kainit, 1 part; acid phosphate, 1 part.
[2] Average of all results by adding HCl to water extract, 4.65% K_2O.
[3] Average of all results by omitting HCl to water extract, 4.64% K_2O.
[4] Acid phosphate, 4 parts; K_2SO_4, 1 part.
[5] Average of all results by adding HCl to water extract, 9.05% K_2O.
[6] Average of all results by omitting HCl to water extract, 9.04% K_2O.

COMMENTS BY ANALYSTS.

W. J. Jones, jr.: In commenting on the methods for the determination of potash, I would say our work here indicates that considerable additional investigation might be given to the present official method which review of the proceedings leads me to believe was adopted without as much investigation as should have been required.

In using the official method we find the results decidedly influenced by the temperature of the water, the manner in which it is placed on the sample, the length of time the solution stands before making the determination, and a number of other factors, and so far as I can discover from the proceedings these points were not investigated before the method was finally adopted.

The more we use this method the more we are inclined to feel that the difference in results found between it and the old method is due not so much to more efficient extractions and determinations of potash in the majority of samples but to multiplication of analytical error due to marked reduction in the amount of sample taken and amount used for the determination. A number of other chemists with whom I have discussed this matter seem to have encountered difficulties similar to those we have found in this department. In many cases it is extremely difficult to get duplications on aliquots from the same solution.

E. G. Proulx: The determination by the perchlorate methods (*d*) and (*e*) are on aliquots from the same solutions.

The results by the modified official method on sample No. 2 average 0.16% lower than by the official method, while on sample No. 3 they are nearly the reverse, being 0.13% higher by the modified method.

In two laboratory samples of fertilizers consisting of acid phosphate and muriate of potash the modified official method gave an average of 0.18% lower potash than the official method in one sample and an average of 0.03% higher in the other.

The effect of the addition of 2 cc. concentrated HCl appears uncertain. It is more important to have the solution at the boiling point when the ammonia and ammonium oxalate are added.

The official method using denatured alcohol gave concordant results which were slightly higher than those secured by the official method; Baker & Adamson's analyzed petroleum ether (specific gravity 0.632), boiling point 40° to 60°C., no heavier oils or sulphur present, was used as the denaturing reagent. The denatured alcohol was very unpleasant, affecting the eyes.

Results by the perchlorate methods were unsatisfactory in all samples. The final percipitates contained insoluble matter averaging 0.0017 gram in sample No. 1. In sample No. 2 the insoluble residue by perchlorate method (*d*) was 0.0060 gram and by perchlorate method (*e*) 0.0050 gram, while in sample No. 3 there was 0.0340 gram insoluble residue with method (*d*) and 0.0083 with method No. 2.

The perchlorate method requires a greater amount of time and would certainly prove more expensive per determination than the official method.

Merck's pure perchloric acid (specific gravity 1.12), containing 0.0012 gram $KClO_4$ in 10 cc., was used in the perchlorate method.

Agart Wiberg: The perchlorate method gave in all of the three samples about 0.20% higher results than the official method, which probably was due to a trace of potassium chlorid in the potassium perchlorate with which the alcohol was saturated; 0.0064 gram of $KClO_4$ was found in 10 cc. perchloric acid, and corrections were made for the same.

R. C. Wiley: I found in my work with the perchlorate method that 10 cc. of perchloric acid (specific gravity 1.12) was not a sufficient amount. When only

this amount was added the resulting potash percentage was often too high. I got uniformly good results by adding about 20 cc. of perchloric acid in place of 10 cc., as is called for by the perchlorate method.

Of the two perchlorate methods, I prefer the $Ba(OH)_2$ process. It seems to me that the perchlorate method is preferable to the official method for the determination of potash in commercial potassium salts. I think it possible that after one became well acquainted with the perchlorate method he could make determinations somewhat more rapidly than by the official method. At the present price of perchloric acid, I doubt if the perchlorate method is more economical with respect to reagents used than the official method, since the platinum can be readily recovered.

I do not think ordinarily the addition of HCl in the water extract influences the results.

W. D. Richardson: We were unable to obtain a supply of perchloric acid and were therefore unable to complete the work on the perchlorate method.

In regard to a comparison of method (*a*) and method (*b*), we do not find that the addition of 2 cc. of hydrochloric acid makes any difference in the results obtained. Our results obtained in using denatured alcohol in method (*c*) as compared with ethyl alcohol in method (*a*) are practically identical.

P. L. Hibbard: The methods sent by the associate referee were closely followed. Omission of boiling the water extract with HCl in method (*b*) seems to be a desirable simplification, without sacrifice of accuracy. The use of denatured alcohol seems permissible, although it has given me slightly lower results. Perhaps it may have contained a little more water, which would account for the difference. From other experiments I have made, I judge that it would be better to use stronger than 80% alcohol, whether denatured or not, for washing K_2PtCl_6.

My results with the perchlorate methods are very unsatisfactory, for reasons unknown to me. The precipitate formed from impure solutions seems to contain foreign substances not removable by 95% alcohol + $KClO_4$. Resolution and reprecipitation with more $HClO_4$ gives a pure precipitate of $KClO_4$.

The $Ba(OH)_2$ process (*e*) for removing sulphate is simpler, but less reliable in my hands. The perchloric acid used gave no appreciable blank for K_2O.

Ninety-five per cent alcohol saturated with $KClO_4$ is not a satisfactory wash for purifying the precipitate of $KClO_4$ on account of the great variation in solubility of $KClO_4$ with change of temperature; also, because in most cases it causes a precipitate of $KClO_4$ in the filtrate which contains $HClO_4$. Alcohol 99% + 0.2% $HClO_4$ seems to me a much better wash.

In using the 95% alcohol + $KClO_4$ for second washing after the precipitate had once been dried and weighed, I more frequently found gain instead of loss in weight. This seems to be due to deposition of $KClO_4$ in filter and precipitate on second washing. If the wash is allowed to percolate slowly through the filter there is likely to be gain in weight, but if it is drawn rapidly through by suction, there is less probability of gain. With pure KCl the perchlorate method has given me nearly theoretical results, but when $BaCl_2$ or NaCl is present in considerable amount, results are high. On account of the necessity for removing sulphate before applying the perchlorate determination, I find this method much slower and less accurate than the platinum method; and when platinum is recovered, as it easily may be, I fancy the latter method is cheaper.

Reprecipitation was done as follows:

Results of reprecipitation.

[Same solution of sample No. 1 used for all these determinations.]

	$KClO_4$ FOUND			
	A	B	C	D
	gram	*gram*	*gram*	*gram*
First result	0.1812	0.1860	0.1850	0.1820
After reprecipitation	0.1773	0.1820	0.1795	0.1810
Again reprecipitated	0.1782	0.1843	0.1800	0.1822

Gooch crucibles were used to collect the precipitate. After the first determination, the crucibles were washed out, dried, weighed; the filtrate evaporated with more $HClO_4$, precipitate filtered, dried, and weighed as at first.

By this process it was expected to get rid of any insoluble or other impurities contained in the first precipitate of $KClO_4$. Above are some of the results on one sample; not very encouraging. Numerous trials of this plan indicate that it may serve to approximate correct results when the first result is too high, due to various impurities.

W. A. Davis: Hydrochloric acid does not appreciably affect the results. If any difference is caused in this way it is certainly less than that caused by other factors. I think there is no doubt the difference arises from difference of sampling. With the 5 grams which I used, it is impossible to insure strict equality in the samples analyzed.

When accurately carried out there is no doubt that the two processes of the perchlorate method give identical results. In my experience it is more difficult, unless very special care is exercised, to obtain concordant and trustworthy results by the barium chlorid process than by the barium hydroxid process, for the following reasons:

(1) It is very difficult to insure that, after a treatment with sulphuric acid, only the quantity of barium chlorid exactly necessary for the precipitation is used. It often happens that a slight excess of barium chlorid is added, which then necessitates the use of considerably more perchloric acid than the 10 cc. specified in the directions in order to keep the whole of the barium in a form of soluble perchlorate. If only 10 cc. of perchloric acid is used, some of the excess of barium chlorid remains unconverted to perchlorate and is precipitated as insoluble barium chlorid when alcohol is added, so that the potassium perchlorate weighed is contaminated by barium chlorid; barium can then be detected in the potassium perchlorate after the latter has been dried and weighed. In some cases I have had the results 30% to 50% high by this cause. In such cases the impure potassium perchlorate on the Gooch should be dissolved in hot water and again evaporated with 5 cc. of perchloric acid, the usual method of collecting the salt being proceeded with. This method generally gives approximately correct results, but frequently the result is a trifle low in such cases owing to a slight loss in the additional manipulation.

In all cases, whether the barium chlorid or barium hydroxid process is used, the potassium perchlorate weighed should always be dissolved in hot water after the analysis and tested for barium by adding sulphuric acid.

(2) In general I find it more difficult to get a perfectly clear solution for the final treatment with perchloric acid by the barium chlorid process than by the barium hydroxid process. After precipitating with barium chlorid it is generally necessary to allow the hot solution to stand for a few hours in order to get a precipitate which filters well and gives an absolutely clear filtrate. In the barium

hydroxid process the water extract after ignition usually gives an absolutely clear filtrate at once. On this account it is more rapid than the barium chlorid process.

(3) Using the barium hydroxid process, the amount of perchlorate acid prescribed is always sufficient to turn the whole of the barium in solution into soluble perchlorates and at the same time convert all the potash salts into perchlorate. There is never any uncertainty such as exists in the barium chlorid process, according to my experience, whether some barium chlorid may be present in the potassium perchlorate.

Considerable error may be caused, sometimes amounting to 0.0050 to 0.0060 gram in the perchlorate weighed, owing to the presence of sulphates or sulphuric acid in the perchloric acid used. If this impurity is present when the 5 cc. of perchloric acid is added to the solution used for analysis, after treatment with barium hydroxid or barium chlorid a slight percipitate or turbidity of barium sulphate appears as the solution is evaporated, owing to the interaction of the barium and sulphuric acid. I found that the perchloric acid obtainable from the dealers now frequently contains so much sulphuric acid as to give a precipitate of 5 to 6 milligrams barium sulphate per 10 cc.

As a check to this source of error, the potassium perchlorate weighed in the Gooch should, after the analysis, be dissolved away by washing with about 300 cc. of boiling water. After drying at 100° C. the Gooch should be weighed and its weight compared with that before collecting the perchlorate. If there is any increase, the second weight of the Gooch should be used to calculate the result, the weight of true perchlorate being thus determined by the loss of weight after washing with water.

In the barium hydroxid process special care should be taken not to heat too strongly during the ignition. The heat should always be well below a red heat, so as to avoid any loss of potash by volatilization.

Care must, of course, be taken not to evaporate the first solution to which barium hydroxid has been added in the same hood as those in which the final solutions containing perchloric acid are being evaporated. The former solutions give off ammonia which would be absorbed by the perchloric acid and add to the weight of the perchlorate finally obtained.

E. E. Vanatta: Perchlorate method required more time than the official method. Four rewashings were required to secure constant weight. We have not the data to give exact cost of recovering the platinum used, but the cost, we believe, is less than the cost of perchloric acid.

In regard to omitting the addition of 2 cc. of HCl and boiling, as in the official method, the results were practically identical with sample No. 3. Slightly higher results were secured with sample No. 2 when the addition of 2 cc. of HCl was omitted. However, this may have been partly due to the amount of potash washed out of the sample.

DISCUSSION OF METHODS AND RESULTS.

THE PERCHLORATE METHOD.

The details of the barium chlorid process of the perchlorate method studied this year are the same as last year except the Davis method of collecting the final precipitate and washing the same were carried out. The barium hydroxid process was devised by W. A. Davis, Rothamsted (England) Experiment Station, who sent the details of manipulation.

While the results by the perchlorate method show a little better agreement than they did last year, they are far from being satisfactory.

On sample No. 1 the maximum percentage found was 12.85, while the minimum was 11.93; an extreme variation of 0.92.

On sample No. 2 by the barium chlorid process: Maximum, 5.47; minimum 4.91; an extreme variation of 0.56. Barium hydroxid process: Maximum, 5.32; minimum, 4.84; an extreme variation of 0.48.

On sample No. 3 by the barium chlorid process: Maximum, 8.87; minimum, 8.48; an extreme variation of 0.39. Barium hydroxid process: Maximum, 8.81; minimum, 8.13; an extreme variation of 0.68. The above figures are taken from averages of coöperating chemists.

While the general average by the two processes of the perchlorate method seem to agree fairly well with the official method, it can readily be seen from Tables 1 and 2 that the results are very discordant.

The perchlorate method has now been studied by the association for three successive years, and an examination of the data during these years shows that while a few chemists get good results by it, in comparison with the official method, there are unquestionably difficulties connected with the details of the process which greatly affect its reliability in the hands of the average analyst. It appears that only by continued repetition can any degree of accuracy be obtained by either of the processes. This is not the case with the official method.

It appears to me that this method is certainly no gain in time over the official method. In fact it takes a much longer time to carry on the process. As it cannot be applied in the presence of sulphates, they must be removed by the addition of barium chlorid or barium hydroxid. This requires an extra filtration. After this filtration, the filtrate, amounting to from 100 cc. to 150 cc., is evaporated with perchloric acid. So it takes a considerably longer time to make this second evaporation than the second evaporation of the official method. The barium hydroxid process is shorter and easier to handle than the barium chlorid process. The results by the two processes are practically the same.

Since perchloric acid is expensive and platinum is easily and cheaply recovered, the perchlorate method is, in my mind, as expensive as the platinum method, especially when the longer time it takes to carry on a series of determinations by the former is considered.

In justice to the method, however, I believe for the determination of potash in materials of small potash content, such as soil and plant ashes, it may be used with success.

In view of the fact that the results during the past three years have been so variable, the details of manipulations so difficult to handle, that there is no gain in time over the official method by its use, and the comments by coöperating chemists have been so generally unfavorable, it

would seem desirable that work on this method be held in abeyance for the present.

THE USE OF DENATURED ALCOHOL FOR WASHING POTASSIUM CHLOROPLATINATE.

The use of denatured alcohol, Formula 1,[1] for washing K_2PtCl_6 gives practically identical results in every case reported in comparison with ethyl alcohol.

Table 1 shows for sample No. 2 an average of 5.07% K_2O by using 80% ethyl alcohol and 5.06% K_2O by using 80% denatured alcohol. Table 2 shows for sample No. 3 an average of 8.55% K_2O with ethyl alcohol and 8.53% K_2O with denatured alcohol. The results reported last year using denatured alcohol were as satisfactory as results reported this year.

As pointed out in the report of the associate referee last year, denatured alcohol, Formula 2,[1] cannot be used as a wash for K_2PtCl_6 for the reason that the pyridin, one of the denaturing agents, is precipitated by platinic chlorid. It can be tested for the presence of pyridin by adding a few drops of platinic chlorid to about 25 cc. of the alcohol. If a precipitate forms after standing about ten minutes it shows the presence of pyridin, and therefore cannot be used for washing K_2PtCl_6.

THE MODIFIED OFFICIAL METHOD.

The average results by the official and the modified official methods for sample No. 2 as shown in Table 1 give the same, 5.07% K_2O. Sample No. 3 as shown in Table 2 gives 0.03% K_2O higher by the modified official method. Tables 3, 4, and 5 show some interesting results on the use of hydrochloric acid to the water extract. They were reported by Davis and Hibbard. The figures obtained with these samples certainly show that the addition of hydrochloric acid does not lead to higher results. Table 4 shows in a case of the mixture of 1.25 grams kainit and 1.25 grams acid phosphate that the average of the three results using hydrochloric acid is practically identical with the average attained when acid is not used. In the case of 4 grams kainit and 2 grams acid phosphate, the average result with hydrochloric acid added is 0.14% lower than the result without the acid. Results reported by Hibbard (Table 5) also show practically identical results by both methods.

If the addition of hydrochloric acid to the water extract in any way affects the results on these samples, the difference is so slight that it is completely obscured by the usual error of manipulation.

[1] U. S. Int. Rev. Reg. No. 30 (rev. Aug. 22, 1911), p. 45.

Therefore, since the results of last year and this year have been practically the same by adding or omitting hydochloric acid, its addition is an unnecessary operation. It interferes with the volumetric determination of chlorin, which in many laboratories has been made in potash solutions.

RECOMMENDATIONS.

It is recommended—

(1) That further work be discontinued on the perchlorate method until it has been so modified as to make it of more practical value.

(2) That 80% by volume denatured alcohol, Formula 1 (U. S. Int. Rev. Reg. No. 30 (rev. Aug. 22, 1911), p. 45) may be used for washing potassium chloroplatinate.

(3) That the official method of making solutions with potash salts and mixed fertilizers be revised to read as follows:

Weigh 2.5 grams upon a 12.5 cm. filter paper and wash with successive small portions of boiling water into a 250 cc. graduated flask to a volume of about 200 cc. In the case of mixed fertilizers, add to the hot solution a slight excess of ammonium hydroxid and then sufficient ammonium oxalate to precipitate all the lime present; cool, dilute to 250 cc., mix, and pass through a dry filter.

REPORT ON SOILS.

By J. W. Ames (Agricultural Experiment Station, Wooster, Ohio), *Referee*.[1]

The instructions for work on soils followed the recommendations made in 1914 and included a study of methods for inorganic carbon, total carbon, and lime requirement. Six samples were sent out to a number of collaborators, but results are available from five laboratories only, including that of the referee.

INORGANIC CARBON.

An accurate measure of the inorganic carbon content of soils is essentail in certain soil investigations. Since the method commonly practiced of boiling with acid does not give reliable results, it is important that a more satisfactory procedure be adopted to replace the method for carbon dioxid in soils, the removal of the method having been recommended and approved at the 1914 meeting.

The object of the work on inorganic carbon was to determine the efficiency of the several methods for decomposing all the soil carbonates, whether naturally present or artificially supplied, without attacking the organic matter.

[1] Presented by W. W. Skinner.

DESCRIPTION OF SAMPLES.

Two soils were selected, one with a low organic-matter content and supposedly free from carbonates, while the other has approximately 3% organic matter and contains a natural supply of carbonates.

To portions of each of these soils, carbonates in the form of high calcium limestone and dolomitic limestone were added, while one portion of each soil received no addition of carbonates. The percentage of inorganic carbon in the soil, based on the composition and amounts of carbonates added, is as follows:

No. 1.—Soil supposed to be free from carbonates.
No. 2.—Soil No. 1 + limestone to make 0.0290% inorganic carbon.
No. 3.—Soil No. 1 + dolomite to make 0.0285% inorganic carbon.
No. 4.—Soil No. 1 + dolomite to make 0.2241% inorganic carbon.
No. 5.—Black clay soil containing natural supply of carbonates.
No. 6.—Soil No. 5 + dolomite to make 0.1425% inorganic carbon in excess of that present in soil No. 5.

The limestone and dolomite added to the soils was ground to pass a 100-mesh sieve and the carbonate content determined. The soils were reduced in a porcelain ball mill to a fineness of less than one-half millimeter. After mixing the finely ground limestone with the soil, the mixtures were reground for two hours. The analytical results for the soils to which carbonates were added indicate that a thorough mixture of the limestone materials and soil was secured by this treatment. In the preparation of soil samples for analysis, carbonates naturally present would not be more finely reduced than the carbonates in the several mixtures of soil and carbonates.

INSTRUCTIONS FOR INORGANIC CARBON.

Use 20 grams of samples 1, 2, 3, and 5; 10 grams of samples 4 and 6.

Method A.—Boiling soil with 1 to 50 hydrochloric acid under reduced pressure as suggested by Marr.[1]

Place soil in suitable flask which will withstand vacuum of approximately 70 cm. Add 80 cc. carbon-dioxid-free distilled water, mix thoroughly, connect to apparatus and start suction. When air has been removed from apparatus and vacuum of 65 to 75 cm. obtained, run in through separatory funnel 20 cc. dilute hydrochloric acid (2 cc. hydrochloric acid (specific gravity 1.19) to 18 cc. of water). Boil for 30 minutes. Bottom of flask should be about three-fourths of an inch above gauze protecting it from free flame. If liquid is drawn up condenser tube, flame should be lowered.

Carbon dioxid evolved is absorbed in a sodium hydroxid solution made from sodium, 25 cc. of 4% sodium hydroxid and sufficient water to cover glass beads in absorbing tower. Relieve vacuum, wash out contents of absorbing tower with 250 cc. carbon-dioxid-free water, using 25 cc. portions, and titrate.

---

[1] J. Agr. Sci., **3**: (2) 155.

Titration: For the assistance of those who have had no experience with the Brown & Escombe double titration method, the following details are given:

Add 1 cc. phenolphthalein to solution and run in normal hydrochloric acid until pink color begins to fade, then add N/20 hydrochloric acid to complete disappearance of color. Take no account of N/1 or N/20 acid used. When end point is reached, add two drops of methyl orange solution (1 gram per 1,000 cc.) and titrate with N/20 hydrochloric acid until lemon color of alkaline methyl orange just approaches distinct pink color. Take reading of N/20 acid and subtract correction obtained from blank determination run under same conditions. 1 cc. N/20 hydrochloric acid = 0.0022 gram carbon dioxid. In this titration it will be necessary for each analyst to establish and adhere strictly to a constant end point for both indicators. It will be well for those not familiar with the titration, to practice on a 4% sodium-hydroxid solution containing small amount of sodium carbonate.

Method B.—Modified procedure proposed by McIntire and Willis[1] using 1 to 10 hydrochloric acid and constant agitation at room temperature.

Method C.—Boiling soil with 1 to 10 hydrochloric acid for 30 minutes. Carbon dioxid evolved is absorbed and titrated as in Methods A and B.

BLANK DETERMINATION ON SOIL AFTER REMOVAL OF CARBONATES.

In order to apply correction for possible action of acid on organic matter in three procedures used, it will be necessary to remove carbonates from sample 5. The blank determination on sample 5 after removal of carbonates will also apply to sample 6. Sample 5 originally contained carbonates. Sample 6 is same soil as 5, but has had carbonates added to it.

Determination of inorganic carbon in sample 1, which, so far as is known, does not contain carbonates, will serve as blank for samples 2, 3, and 4.

Removal of carbonates from sample 5.—It is suggested that a method similar to the following be used.

Place 20 grams of soil in a 250 cc. beaker, add 100 cc. of 1 to 10 hydrochloric acid and stir. Allow to stand for two hours, or longer if necessary, stirring occasionally. Then filter through blue ribbon filter paper folded in Büchner funnel. The paper can be folded into a cylindrical shape to fit the funnel by forming it over cork of the same size as inside diameter of funnel. Wash soil a few times to remove as much acid as possible, using carbon-dioxid-free water. Continue suction until all excess moisture has been drawn off soil, then transfer soil from paper to apparatus and proceed to evolve carbon dioxid as outlined under the three procedures.

RESULTS FOR INORGANIC CARBON.

The data for inorganic carbon are presented in the following tables: Table 1 contains results for the association samples. Results for these same soils by modifications of methods outlined in instructions are given in Table 2.

[1] J. Ind. Eng. Chem., (1915), **7**: (3) 226.

TABLE 1.

Inorganic carbon, per cent in air-dry soil.

ANALYST	SAMPLE 1			SAMPLE 2		
	Method[1]			Method[1]		
	A	B	C	A	B	C
C. J. Schollenberger, Ohio.....	0.0006	0.0006	0.0096	0.0303	0.0282	0.0372
	0.0009	0.0006	0.0096	0.0294	0.0288	0.0372
	0.0006	.....	0.0096	0.0288	0.0282	.....
	.....	.....	0.0093	0.0303	.....	.....
Average.....	0.0007	0.0006	0.0096	0.0298	0.0284	0.0372
	0.0007	0.0006	0.0096	0.0007	0.0006	0.0096
Less blank.....	0.0000	0.0000	0.0000	0.0291	0.0278	0.0276
L. G. Willis, Tennessee.....	0.0066	0.0024	0.0147	0.0335	0.0287	0.0432
	0.0054	0.0018	0.0140	0.0340	0.0295	0.0451
	.....	0.0023	0.0151	.....	0.0292	0.0443
Average.....	0.0060	0.0022	0.0146	0.0338	0.0291	0.0442
	0.0060	0.0022	0.0146	0.0060	0.0022	0.0146
Less blank.....	0.0000	0.0000	0.0000	0.0278	0.0269	0.0296
W. H. Sacks, Illinois.....	0.0006	0.0037	0.0098	0.0232	0.0235	0.0367
(Reported by E. Van Alstine)	0.0009	0.0022	0.0104	0.0262	0.0196	0.0355
	.....	0.0014	.....	0.0254	0.0199	0.0350
Average.....	0.0008	0.0024	0.0101	0.0249	0.0210	0.0357
	0.0008	0.0024	0.0101	0.0008	0.0024	0.0101
Less blank.....	0.0000	0.0000	0.0000	0.0241	0.0186	0.0256
W. L. Latshaw, Kansas.....	0.0036	.....	0.0300	0.0243	.....	0.0542
	0.0025	.....	0.0300	0.0238	.....	0.0548
	0.0033	.....	0.0259	0.2030	.....	0.0545
	0.0028	.....	.....	.....	.....	.....
Average.....	0.0030	.....	0.0286	0.0237	.....	0.0545
	0.0030	.....	0.0286	0.0030	.....	0.0286
Less blank.....	0.0000	.....	0.0000	0.0207	.....	0.0259
O. F. Jensen, Michigan.....	.....	.....	.....	0.0278	.....	.....
	.....	.....	.....	0.0215	.....	.....
Average[2].....	.....	.....	.....	0.0246	.....	.....

[1] A, Marr method; B, McIntire method; C, boiling with 1 to 10 hydrochloric acid for 30 minutes.
[2] Blank on soil not stated.

TABLE 1—Continued.

ANALYST	SAMPLE 3			SAMPLE 4		
	Method[1]			Method[1]		
	A	B	C	A	B	C
C. J. Schollenberger, Ohio.....	0.0294	0.0267	0.0372	0.2172	0.2142	0.2225
	0.0300	0.0258	0.0372	0.2172	0.2124	0.2232
	0.0300	0.0270	.....	0.2208	0.2124	.....
	0.0288	0.0276	.....	0.2220	0.2130	.....
	.....	.....	.....	0.2232	.....	.....
Average.....	0.0296	0.0268	0.0372	0.2201	0.2130	0.2229
	0.0007	0.0006	0.0096	0.0007	0.0006	0.0096
Less blank.....	0.0289	0.0262	0.0276	0.2194	0.2124	0.2133
L. G. Willis, Tennessee.....	0.0330	0.0275	0.0410	0.2115	0.2132	0.2253
	0.0316	0.0289	0.0410	0.2107	0.2121	0.2287
	.....	0.0292	.....	.....	0.2105	.....
	.....	0.0270	.....	.....	.....	.....
Average.....	0.0323	0.0281	0.0410	0.2111	0.2119	0.2270
	0.0060	0.0022	0.0146	0.0060	0.0022	0.0146
Less blank.....	0.0263	0.0259	0.0264	0.2051	0.2097	0.2124
W. H. Sacks, Illinois.....	0.0278	0.0172	0.0370	0.2070	0.1621	0.2163
(Reported by E. Van Alstine)	0.0278	0.0185	0.0383	0.2082	0.1537	0.2226
	.....	0.0187	.....	.....	0.1531	0.2208
Average.....	0.0278	0.0181	0.0376	0.2076	0.1563	0.2199
	0.0008	0.0024	0.0101	0.0008	0.0024	0.0101
Less blank.....	0.0270	0.0157	0.0275	0.2068	0.1539	0.2098
W. L. Latshaw, Kansas.....	0.0248	.....	0.0551	0.2259	.....	0.2545
	0.0235	.....	0.0551	0.2229	.....	0.2552
	0.0235	.....	0.0548	0.2246	.....	0.2558
Average.....	0.0240	.....	0.0551	0.2245	.....	0.2552
	0.0030	.....	0.0286	0.0030	.....	0.0286
Less blank.....	0.0210	.....	0.0265	0.2215	.....	0.2266
O. F. Jensen, Michigan.....	0.0305	.....	.....	0.2070	.....	.....
	0.0286	.....	.....	0.1985	.....	.....
Average[2].....	0.0295	.....	.....	0.2027	.....	.....

[1] A, Marr method; B, McIntire method; C, boiling with 1 to 10 hydrochloric acid for 30 minutes.
[2] Blank on soil not stated.

TABLE 1—Continued.

ANALYST	SAMPLE 5			SAMPLE 6		
	Method[1]			Method[1]		
	A	B	C	A	B	C
C. J. Schollenberger, Ohio.....	0.1440	0.1158	0.1584	0.2844	0.2304	0.2940
	0.1427	0.1242	0.1584	0.2760	0.2376	0.2928
	0.1482	0.1236	.....	0.2738	.....	.....
	0.1467	.....	.....	0.2700	.....	.....
Average.....	0.1454	0.1212	0.1584	0.2759	0.2340	0.2934
	.....	.....	0.0099	.....	.....	0.0099
Less blank.....	0.1454	0.1212	0.1485	0.2759	0.2340	0.2835
L. G. Willis, Tennessee.....	0.1498	0.1270	0.1656	0.2785	0.2410	0.2962
	0.1500	0.1320	0.1645	0.2797	0.2527	0.2941
	.....	0.1222	0.1657	.....	0.2259	.....
	.....	0.1243	.....	.....	0.2512	.....
	.....	0.1222	.....	.....	0.2152	.....
	.....	0.1251	.....	.....	0.2555	.....
	.....	.....	.....	.....	0.2295	.....
	.....	.....	.....	.....	0.2488	.....
Average.....	0.1499	0.1272	0.1646	0.2791	0.2400	0.2951
	0.0022	0.0009	0.0173	0.0022	0.0009	0.0173
Less blank.....	0.1477	0.1263	0.1473	0.2769	0.2391	0.2778
W. H. Sacks, Illinois.....	0.1449	0.1119	0.1515	0.2721	0.2221	0.2700
(Reported by E. Van Alstine)	0.1419	0.1053	0.1559	0.2727	0.2267	0.2784
	0.1407	0.1062	0.1593	.....	0.2185	0.2805
	0.1405	.....	.....	.....	.....	0.2811
Average.....	0.1420	0.1078	0.1556	0.2724	0.2224	0.2775
	0.0014	0.0023	0.0079	0.0014	0.0023	0.0079
Less blank.....	0.1406	0.1055	0.1477	0.2710	0.2201	0.2696
W. L. Latshaw, Kansas.....	0.1285	.....	0.1722	0.2768	.....	0.3408
	0.1285	.....	0.1722	0.2768	.....	0.3392
	0.1278	.....	0.1718	0.2768	.....	0.3380
	.....	.....	.....	0.2768	.....	.....
Average.....	0.1283	.....	0.1721	0.2768	.....	0.3390
	.....	.....	0.0346	.....	.....	0.0346
Less blank.....	0.1283	.....	0.1375	0.2768	.....	0.3044
O. F. Jensen, Michigan.....	0.1298	.....	.....	0.2481	.....	.....
	0.1309	.....	.....	0.2185	.....	.....
Average[2].....	0.1303	..	.....	0.2333	.....	.....

[1] A, Marr method; B, McIntire method; C, boiling with 1 to 10 hydrochloric acid for 30 minutes.
[2] Blank on soil not stated.

TABLE 1—Continued.

ANALYST	BLANK ON SAMPLE 5 AFTER EXTRACTION WITH 1 TO 10 HYDROCHLORIC ACID		
	Method[1]		
	A	B	C
C. J. Schollenberger, Ohio.....	.....	.....	0.0096
	.....	.....	0.0102
Average.....	.....	.....	0.0099
L. G. Willis, Tennessee.....	0.0023	0.0009	0.0179
	0.0020	0.0009	0.0168
Average.....	0.0022	0.0009	0.0173
W. H. Sacks, Illinois.....	0.0007	0.0020	0.0077
(Reported by E. Van Alstine)	0.0021	0.0025	0.0081
Average.....	0.0014	0.0023	0.0079

[1] A, Marr method; B, McIntire method; C, boiling with 1 to 10 hydrochloric acid for 30 minutes.

TABLE 2.

Miscellaneous results for inorganic carbon by modifications of Methods A, B, and C.

ANALYST	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6
L. G. Willis, Tennessee: Method A, using 3 to 100 hydrochloric acid.	.....	.....	.....	0.2182	.....	0.2797
	.....	.....	.....	0.2162	.....	0.2840
Average.....	.....	.....	.....	0.2172	.....	0.2819
	.....	.....	.....	0.0060	.....	0.0022
Less blank on soil.....	.....	.....	.....	0.2112	.....	0.2797
C. J. Schollenberger, Ohio: Method B, shaking 1¾ hours.....	.....	.....	.....	.....	.....	0.2748
	.....	.....	.....	.....	.....	0.2688
Average.....	.....	.....	.....	.....	.....	0.2718
Method C, carbon dioxid measured....	0.0103	0.0369	0.0373	0.2313	0.1608	0.2980
	0.0083	.....	.....	.....	.....	.....
Average.....	0.0093	.....	.....	.....	.....	.....
	0.0093	0.0093	0.0093	0.0093	0.0100	0.0100
Less blank on soil.....	.....	0.0276	0.0280	0.2220	0.1508	0.2880
W. H. Sacks, Illinois (reported by E. Van Alstine); Boiling 2 minutes with 1 to 1 hydrochloric acid; carbon dioxid measured.	0.0036	0.0288	0.0316	0.2203	0.1482	0.2804
	0.0046	0.0288	0.0311	0.2203	0.1482	0.2823
	.....	.....	.....	.....	0.1466	.....
	.....	.....	.....	.....	0.1476	.....
Average.....	0.0041	0.0288	0.0314	0.2203	0.1477	0.2814
	0.0041	0.0041	0.0041	0.0041	0.0045	0.0045
Less blank on soil.....	.....	0.0247	0.0273	0.2162	0.1432	0.2769

COMMENTS OF COLLABORATOR.

E. Van Alstine: Comparison of figures would indicate that the Marr method gives results perhaps more nearly correct, for with sample 1, which is supposed to contain no carbonates, it gives much the lowest results, indicating that it decomposes the least amount of organic matter, while with soils known to contain carbonates, it gives results that compare closely with the method of boiling at atmospheric pressure with hydrochloric acid.

The McIntire method, on the other hand, not only seems to decompose a fairly large amount of organic matter, but with soils containing large amounts of carbonates the results are apparently too low, indicating that the method not only attacks organic matter but does not decompose all of the carbonates present.

Boiling for 30 minutes with 1 to 10 hydrochloric acid at atmospheric pressure decomposes more organic matter than it should; but when this, as found in samples 1 and 5 after removal of carbonates, is applied as a correction, results on the other samples compare closely with all except the MacIntire method. The same is true with the method of boiling for 2 minutes in 1 to 2 hydrochloric acid, but much less organic matter is attacked when the same soil is boiled for 30 minutes in a weaker solution. A method, to be practicable, of course must be one with which one need not apply a correction other than that for impurities in the reagents, since it is evident that one can not correctly apply as a correction the inorganic carbon indicated to be present in a soil known to contain none, to other soil containing limestone and which may also contain organic matter more easily or less easily attacked by the reagent. It is also very evident that in practice one can not remove carbonates from a soil "supposedly" by any method, then treat the residue with reagents to be used in the organic carbon determination, applying the apparent carbonates found in this way as a correction. If this is done, the question at once arises, What method shall we use to free the soil of carbonates and at the same time leave the organic matter unattacked, to be acted upon by the reagents in the regular inorganic carbon determination?

If we can use one of these methods for inorganic carbon without applying a correction other than that for impurities in the reagent used, then the Marr method has an advantage, since it attacks organic matter much less than any other method does. One thing which should be tested thoroughly is whether or not the Marr method will liberate all the carbon dioxid from dolomitic limestone which is found in many soils in the northern part of this State, and undoubtedly in other States as well. I may say, in this connection, that the method of boiling for 2 minutes in 1 to 2 hydrochloric is much quicker, more easy to manipulate, and for comparative results for most soils is accurate enough so that one seems justified in using it in preference to the Marr method.

In certain peat soils which contain a certain amount of acid decomposed organic matter, I have found that results by the Marr method are more trustworthy.

L. G. Willis: I believe, judging from the color of the acid extract of sample 5 and the slight activity on the organic matter due to treatment in Methods A and B, that the use of 1 to 10 hydrochloric for extraction causes some decomposition of the organic matter, and the blanks obtained are, therefore, too low. I question whether the variations due to this probable error in the blank are constant for all methods.

C. J. Schollenberger: The results this year confirm those of 1914, in that the MacIntire method for inorganic carbon does not give satisfactory results with soils containing any considerable quantity of natural carbonates. The cause is probably the practical impossibility of grinding the sample to a sufficient degree of fineness

to be completely decomposed by cold acid, or the well-known resistant character of dolomitic limestone when not ground to an impalpable powder. The Marr method has given fairly satisfactory results; very good, indeed, when compared with Method C, using the double titration procedure for the estimation of the evolved carbon dioxid, with the single exception of sample 6. The somewhat low results by the Marr method on this sample indicate that it may sometimes be advisable to increase slightly the strength of the acid over the standard 1 to 50. When the results by Method C, using the double titration method, are compared with those for Method C, measuring the carbon dioxid, the results are found to be low in the cases of samples 4, 5, and 6. This is no doubt due to the well-known inaccuracy of the double titration method when used for the estimation of rather large quantities of carbon dioxid.

Repeated trials with both Methods, A and C, using about 0.2 gram Iceland spar and estimating the evolved carbon dioxid by the double-titration method, gave a recovery ranging from 95% to 99%. In a trial with the same sample of Iceland spar, using the Marr apparatus, 1 to 50 hydrochloric acid and boiling under vacuum of 65 cm., but dispensing with the bead tower and substituting a Meyer bulb tube with barium hydroxid solution, filtering, and titrating the precipitated barium carbonate,[1] a perfect recovery was obtained. Lack of time prevented a further study of this procedure as applied to soils.

W. L. Latshaw: In Method A, boiling under reduced pressure, we found that half-pint milk bottles were very satisfactory to withstand the pressure. This method of determining carbonates in soil is very satisfactory, and we plan to use it in our survey work.

DISCUSSION OF RESULTS.

The results reported by collaborators who had previous experience with the methods from special studies on determination of soil carbonates having been made in their laboratories show a fairly close agreement where the same method was used, after the blank determination for each method is applied.

Soil 1 is from cultivated plots of the Ohio Experiment Station and has never been limed. This soil is derived from sandstone and shales, and, so far as is known, does not contain either a natural or artificial supply of calcium or magnesium carbonates. Boiling this soil for 30 minutes with 1 to 10 hydrochloric acid gives a higher figure for inorganic carbon than is shown by boiling with 1 to 50 acid under reduced pressure (Method A), or with 1 to 10 hydrochloric acid at room temperature (Method B). This points out the effect of boiling with acid on the organic matter of the soil in the methods ordinarily employed for the determination of inorganic carbon. Boiling soil 1 with 1 to 1 hydrochloric acid for 2 gives a lower figure than is obtained by boiling with acid one-tenth as strong for 30 minutes. This indicates that the action on the organic matter is due more to the heating at 100°C. than it is to the strength of the acid. The blank obtained by boiling soil 1 for 2 minutes

[1] J. R. Cain. J. Ind. Eng. Chem., **6**: 465.

with 1 to 1 hydrochloric acid is much greater than the blank shown by boiling with 1 to 50 acid with reduced pressure (Method A).

Results for soils 2, 3, and 4, in which the added carbonates were in a finely divided condition, show a more complete decomposition and recovery of carbonates by both Methods A and B than is obtained from soil 5, which contains a natural supply of carbonates.

In the case of soil 5, having a natural supply of carbonates, and soil 6, which contains added carbonates from dolomite in addition to the natural content of soil 5, the results obtained by boiling with 1 to 50 acid under reduced pressure agree with those by boiling for 30 minutes with 1 to 10 acid after subtracting the blank, and are considerably higher than results obtained by treating with 1 to 10 acid at room temperature (MacIntire method), which has not been sufficient to decompose the calcium and magnesium carbonates.

The blank determination on the soil previously extracted with acid to remove carbonates gives some indication of the action of the procedure employed on the organic matter, but there is no certainty that by the treatment with acid for the removal of the carbonates a portion of the organic matter which would be easily acted upon is not removed by the acid treatment. That there is a considerable amount of carbon from organic sources obtained by boiling the soil with 1 to 10 acid for 30 minutes after removal of carbonates is evident from the large blank obtained. When this blank is applied as a correction to results by this method, the figures obtained agree closely in most instances with the results by Method A. It is not probable that there is any appreciable action on the organic matter by either Methods A or B. The high figure obtained for the blank in some instances can no doubt be considered partly as a blank on the manipulation of the process rather than being entirely due to the activity of the acid on organic matter.

It will be impossible to decompose the carbonates in soils without producing some slight action on the organic matter. This will be greater for some soils than others, depending upon the nature of the organic matter present. Making a blank determination and applying this as a correction is impracticable. The most satisfactory procedure will be to employ a method which will decompose all the carbonates and at the same time have the least activity on organic matter present.

The Marr method for decomposing soil carbonates seems to fulfill this condition better than any method which has thus far been proposed. The results as a whole indicate that the Marr method is more efficient than the McIntire method for decomposing calcium and magnesium carbonates, whether naturally present or artificially supplied.

The estimation of carbon dioxid evolved from carbonates by titration is not altogether satisfactory. In the double titration procedure there

are sources of error which tend to give low results, especially when the carbonate content of the soil is fairly large. Results by C. J. Schollenberger show a more complete recovery of inorganic carbon from soils 4, 5, and 6 is secured by decomposing the carbonate after absorption in sodium hydroxid and measuring the carbon dioxid.

Instead of absorbing carbon dioxid in sodium-hydroxid solution and making a double titration, more accurate results will be obtained by absorbing carbon dioxid in barium hydroxid, using a Victor-Meyer absorption tube and determining the carbonate by standard methods, either titrating the barium carbonate after filtering and washing, or by making a gravimetric determination.

TOTAL CARBON.

INSTRUCTIONS TO COLLABORATORS.

For determination of total carbon use samples 1 and 5.

Transfer 3 grams of soil into a short-necked Kjeldahl or other suitable flask and connect to same apparatus used for determination of inorganic carbon. Run into flask through separatory funnel 10 cc. chromic-acid solution containing 3.3 grams chromic acid, then 50 cc. concentrated sulphuric acid. The mixture is boiled for

TABLE 3.

Total carbon results.

	SOIL 1	SOIL 5
Combustion with sulphuric and chromic acid; carbon dioxid titrated:		
C. J. Schollenberger, Ohio	0.8000	2.7280
	0.8000	2.7360
	0.8020	2.6800
	0.8040	2.6960
	.....	2.7460
Average	0.8015	2.7172
W. L. Willis, Tennessee	0.8380	2.7270
	0.8300	2.7390
	0.8350	2.7370
	0.8490	2.7370
	0.8430	2.7310
	0.8270	.....
Average	0.8370	2.7340
Combustion with sulphuric and chromic acid; carbon dioxid measured:		
C. J. Schollenberger	0.9010	2.9030
	0.8860	3.0050
	.....	2.8940
Average	0.8940	2.9340
Combustion with copper oxid in furnace, carbon dioxid weighed[1]	0.8800	2.9525
	0.8800	2.9525

[1] The products of combustion were passed over heated copper oxid in a second tube; the residues we tested for carbonate in all cases, with negative results.

30 minutes, during which time a moderate current of carbon-dioxid-free air is drawn through the boiling mixture. Carbon dioxid may be absorbed and titrated as directed under instructions for inorganic carbon. About 5 drops of a 10% solution of sodium thiosulphate should be added to alkali before titration to overcome any effect caused by carrying over of chromic-acid compounds. It will be well for each collaborator to compare method with combustion in furnace or other method for inorganic carbon used in his laboratory.

COMMENTS OF COLLABORATORS.

C. J. Schollenberger: As was the case in 1914, the results for total carbon by the method of wet combustion with sulphuric and chromic acids, estimating the evolved carbon dioxid by double titration, are considerably lower than those obtained by a furnace combustion, absorbing and weighing the evolved carbon dioxid. When a gasometric method is substituted for the double titration procedure, the results obtained by the wet combustion compare fairly well with those obtained by furnace combustion and weighing. Upon comparison of the results for inorganic carbon by Method C, using the double titration and the gasometric methods for estimation of the evolved carbon dioxid and for present purposes considering the latter to be correct, it is found that the average percentage of recovery was about 97.7. A similar comparison of the results for total carbon indicates a percentage of recovery of only 91.8. This would indicate either incomplete absorption of the evolved carbon dioxid, or possibly interference due to the presence of large amounts of sulphate; it was noticed that one-third to one-half the alkali in the absorption tower was invariably neutralized by the acid fumes from the boiling acid in the flask.

DISCUSSION.

While the results for total carbon are insufficient to permit of any definite conclusions being drawn from the work done so far, it is evident that combustion with mixture of chromic and sulphuric acids and determining the carbon dioxid by titrating the absorbing alkali solution gives lower results than are obtained by measuring carbon dioxid resulting from the combustion.

The amount found by measuring the carbon dioxid evolved from the wet combustion agrees closely with that found by combustion of soil in furnace and weighing. This indicates that boiling with a mixture of chromic acid and sulphuric acid, as outlined in the instructions, is sufficient to oxidize the organic matter, but that the lower results are due to errors in the double-titration procedure, when used in combination with the wet-combustion method.

The work on organic carbon was taken up following the recommendation made by the referee on soils for 1913. It does not seem advisable to continue the work, since the standard method of determining organic carbon by combustion, either in current of oxygen or by mixing with copper oxid, and the optional official method are efficient.

Since the figure for total carbon obtained by whatever procedure is employed must be corrected for carbon from carbonates which may be present in the soil, it is important that this correction be based on a more accurate determination than is commonly practiced.

LIME REQUIREMENT.

The instructions sent out suggested that those interested compare two of the more recent of the numerous methods which have been proposed for the estimation of lime requirement, with the Veitch, Hopkins, or other method on soils of known history available for the purpose. It was also stated that sample 1 of the soils for work on inorganic carbon be used. The two methods referred to are the Hutchinson-MacLennan[1] method and a modification of that published by McIntire.[2]

In both these methods the calcium absorbed from the solution of calcium bicarbonate is taken as a measure of the lime requirement.

Some of the collaborators made lime requirement determinations on the association samples to which calcium and magnesium carbonates had been added as stated in Table 1. The results obtained in study of lime requirement methods are given in the following tables:

TABLE 4.

Lime requirement results.

[Average per cent calcium carbonate required.]

ANALYST	SAMPLE	SOIL USED	METHOD			
			Hutchinson-MacLennan	McIntire	Modified McIntire[1]	Jones
		grams				
W. H. Sacks, Illinois (reported by E. Van Alstine).	1	20	0.1563	.....	.....	.....
	1	10	0.1875	0.4020	0.2408	.....
	1	5	0.2900	.....	.....	.....
	2	20	0.0950	0.2918	0.1559	.....
	5	20	0.0200	0.0735 to 0.2735	0.0033 to 0.0266	.....
G. L. Willis, Tennessee.....	1	.....	0.3565	1.1080	.....	.....
W. L. Latshaw, Kansas.....	1	.....	0.1700	.....	.....	.....
	2	.....	0.0438	.....	.....	.....
	3	.....	0.0600	.....	.....	.....
	4	.....	0.0520	.....	.....	.....
	5	.....	[2]0.0252	.....	.....	.....
	6	.....	[2]0.0250	.....	.....	.....
C. J. Schollenberger, Ohio...	1	20	0.2100	.....	.....	.....
	1	10	.....	0.3750	.....	.....
O. F. Jensen, Michigan.....	1	.....	.....	.....	.....	0.2007
	2	.....	.....	.....	.....	0.0963
	3	.....	.....	.....	.....	0.1766
	4	.....	.....	.....	.....	0.1445 to 0.1766
	5	.....	.....	.....	.....	0.0482
	6	.....	.....	.....	.....	0.0321

[1] Excess calcium carbonate determined by boiling for 2 minutes with 1 to 1 hydrochloric acid and measuring carbon dioxid evolved.

[2] Per cent calcium carbonate given up by soil.

[1] Chem. News, Aug. 7, 1914, vol. 110, No. 2854.

[2] J. Ind. Eng. Chem., **7**: (10) 864.

TABLE 5.

Lime requirement results on miscellaneous Illinois soils by methods indicated. (W. H. Sacks and E. Van Alstine, analysts.)

[Average percentage calcium carbonate required.]

SAMPLE NO.	SOIL USED	METHOD			
		Hutchinson-MacLennan	McIntire	Modified McIntire[1]	Hopkins-Pettit
	grams				
1745 (0 to 7 inches)	20	0.148	0.083 + to 0.384	0.1905	0.0185
1746 (7 to 16 inches)	20	0.3415	.....	.....	0.2905
	10	.....	0.240 + to 0.450+	.....	.....
1747 (18 to 40 inches)	20	0.706	.....	.....	.....
	10	0.795	0.303 + to 0.585+	0.7034	0.8090
	5	0.845	0.415 + to 0.560+	0.8432	.....
1748 (0 to 7 inches)	20	0.190	.....	.....	0.0250
	10	0.200	0.322	.....	.....
1749 (7 to 18 inches)	20	0.2155	.....	.....	0.123
1750 (20 to 40 inches)	20	0.3600	.....	.....	0.2815
1751 (0 to 7 inches)	20	0.1265	.....	.....	0.005

[1] Soil and 100 cc. calcium bicarbonate solution evaporated to a thin paste and excess carbonate determined by boiling for 2 minutes with 1 to 1 hydrochloric acid and measuring carbon dioxid evolved.

TABLE 6.

Lime requirements obtained by varying conditions of McIntire method.

SOIL USED TO 100 CC. SOLUTION.	TREATMENT	CALCIUM CARBONATE PER 2,000,000 POUNDS OF SOIL
grams		*pounds*
10	Evaporated to thin paste immediately	7,500
10	Evaporated to dryness immediately	8,200
20	Evaporated to thin paste immediately	5,750
20	Evaporated to dryness immediately	6,300
10	Evaporated to thin paste immediately; to dryness 12 hours later	8,900
10	Soil and solution in contact 12 hours before evaporating to dryness	8,100

COMMENTS OF COLLABORATORS

E. Van Alstine: The Hutchinson-MacLennan method gives much higher results on soils with a small lime requirement, in this case surface soils, than does the Hopkins method; the two methods giving more nearly the same results on subsoils with a large lime requirement. This is also true of the McIntire method. By varying the amount of soil used, the Hutchinson-MacLennan method shows in every test on three soils, 1745, 1747, 1748, that with smaller amounts of soil the lime requirement appears to be higher, the greater variation appearing on soils with a high lime requirement. Thus on soil 1745, varying the size of sample from 20 to 10 grams, causes

a variation from 0.148 to 0.170; on sample 1747 varying the size of sample from 20 to 5 grams causes a variation in apparent per cent of calcium carbonate required from 0.706 to 0.845. Sample 1 sent out this year for referee work shows this same sort of variation. When 20, 10, and 5 gram samples were used, the per cent of calcium carbonate required varied from 0.156 to 0.290. The MacIntire method shows the same sort of variation, the per cent of apparent calcium carbonate requirement of sample 1747 varying from 0.703 to 0.843 with 20 and with 10 gram samples.

It would seem from this fact that when a soil is treated with calcium bicarbonate solution or with calcium carbonate in water or in a salt solution, as I have found by previous work along this line, the amount of carbonate which the soil will decompose and the amount of calcium which the soil will extract and hold is not constant, but varies with the ratio between the amount of soil and amount of carbonates present. This would mean that a soil with a high lime requirement would decompose a larger amount of carbonate, thus in effect weakening the carbonate solution, than would a soil with a low lime requirement, so that in order that the results on such soils be strictly comparable, one should use a larger amount of carbonate with a soil high in lime requirement than with one which has a low requirement, which of course would not be practicable. Moreover, there is no means of knowing the proper amounts of soil and solution to be used in order that the results may represent the truth in regard to the calcium carbonate any soil requires. It is evident that if either method is to be used, arbitrary amounts of soil and solution must be adopted; this then would give only comparative rather than absolute results, and fall short of our needs for an exact method as do other methods now in use. As it is hoped that the method represents what actually takes place in agricultural practice, then it would seem that one should use with the soil sample only as much calcium carbonate as would represent the amount most often used for acid soils.

If one takes 2,000,000 pounds as the standard weight of the surface soil, then to represent a ton application of limestone to the acre would require but 10 milligrams of calcium carbonate, or 10 cc. of the N/50 bicarbonate solution, for a 10-gram sample; for perhaps the most common application of limestone, 2 tons to the acre, this would be but 20 milligrams calcium carbonate or 20 cc. of bicarbonate solution for a 10-gram sample. This would clearly give very much lower results than are obtained by the amounts used in the method as outlined (250 cc.) which represents 25 tons to the acre with a 10-gram sample. The Hutchinson-MacLennan method shows a lime requirement on soils which have a considerable amount of calcium carbonate in them.

Sample 2, which none of the methods used for inorganic carbon shows to contain less than 0.14% calcium carbonate, has, according to this method, a calcium-carbonate requirement of 0.095%, equivalent to an application of nearly a ton of limestone to the acre; while sample 5, which every method for inorganic carbon shows to contain 0.85% or more of calcium carbonate, is shown to have a calcium carbonate requirement of 0.02%, or 400 pounds per acre. This is in accordance with what is indicated by varying the size of the sample, that the greater the amount of calcium carbonate the soil is treated with the more it will decompose and the more calcium it will absorb. McIntire's method shows this same thing, although there is a greater variation in the results obtained. With this method it seems clear that one must subtract the calcium carbonate remaining after the reaction from the sum of the calcium carbonate added in the bicarbonate solution and that indicated to be present in the soil by the method used for determining calcium carbonate in the residue after the reaction, even though one is working with an acid soil, since as much carbon dioxid would be driven off from the soil alone after treatment with bicarbonate solution as would be before treatment.

Making estimations in this way, the McIntire method shows soil 2 to have a calcium carbonate requirement of 0.291% (2.9 tons per acre), while results on soil 5 indicate a lime requirement varying from 0.07% to 0.27%. I may say, in this connection, that results obtained on lime requirement from the calcium carbonate in the residue, also determination by the McIntire method of aëration were not satisfactory, as is shown by comparing results obtained in this way with those in the column under modified McIntire method.

Results are much closer when the remaining carbonate is determined by boiling with hydrochloric acid and measuring the carbon dioxid evolved. Because of the fact that the double titration for bicarbonates is not altogether satisfactory, especially in the hands of chemists not thoroughly familiar with it, the end points not always being distinct, and because with the double titration there are two chances for error, we favor the method of measuring the carbon dioxid which should give results as accurate as those obtained by accurate titrations.

The McIntire method does have an advantage over the Hutchinson-MacLennan in one respect, however. Thus, results for sample 5 show that the soil has actually used up some of the calcium carbonate, but after the reaction there is left in the soil more calcium carbonate than was added, so that while the treatment caused the soil to absorb calcium and decompose the carbonate, there is in the soil from the beginning more than this amount of carbonate and the soil can not be said to be in need of an application of limestone.

Sample 2, which apparently from the inorganic carbon tests does not need an application of limestone, does have, according to the McIntire method, a large lime requirement, and this requirement is more than great enough to require all the limestone in the soil, as found by the McIntire test for inorganic carbon.

In this one respect, that with soils comparatively high in carbonate content there is opportunity to see whether or not the carbonates in that soil are sufficient to satisfy its apparent lime requirement, the method proposed by McIntire seems to be preferable to that of Hutchinson and MacLennan. Yet, even with this advantage, the lime requirement which it indicates must depend upon the use of arbitrary amounts of soil and bicarbonate solution in the test, a condition which should not be necessary in any method of chemical analysis.

C. J. Schollenberger: Varying the amount of soil used and the conditions of evaporation in the McIntire procedure affect the results obtained to an extent which prevents this from being a practicable method. If the evaporation of the soil and calcium bicarbonate solution is carried to dryness, higher results are obtained than if evaporated to a thin paste, as called for in the method. The results also vary with the time required for the evaporation, even when it is carried to the same stage.

On the other hand, a longer contact between soil and bicarbonate solution before beginning evaporation seems to have but a slight effect, provided the conditions during the subsequent evaporation are not varied. These points are brought out in the table included; the soil used was sample 1. This soil has a rather high lime requirement as determined by this method; a 10-gram sample decomposed somewhat more than one-half the calcium bicarbonate contained in 100 cc. of the solution used; a 20-gram sample, then, should use up the entire quantity. As a matter of fact, only about three-quarters of the total calcium carbonate originally in the solution was decomposed when a 20-gram sample was used. The Marr method was used for the determination of residual calcium carbonate. The same objections will no doubt apply to the Hutchinson-MacLennan method, namely, that the results obtained will depend upon a number of factors.

A soil which showed a calcium absorption equivalent to 3,025 pounds calcium carbonate per 2,000,000 as determined by shaking 40 grams soil in 200 cc. solution for 3 hours, gave a figure equivalent to 3,600 pounds calcium carbonate per 2,000,000 when 100 grams of the same soil was shaken with 500 cc. of the same bicarbonate solution for 3 hours, then allowed to stand overnight before filtering and titrating.

For purposes of comparison, the lime requirements as determined by several methods on soil No. 1 are given below.

Lime requirement as pounds calcium carbonate per 2,000,000 soil.

Hopkins-Pettit method	600
Hutchinson-MacLennan method	1,280
McIntire method	7,500
"Vacuum method"	6,200

DISCUSSION.

The results for lime requirement show a wide divergence for the same soil by the several methods used by those who submitted a report on this subject. By varying the proportion of soil used in the Hutchinson-MacLennan method, a calcium-carbonate requirement of from 400 to 5,800 pounds per acre is indicated. The McIntire method also shows the same sort of variation. Results by this method are also influenced considerably by the conditions of evaporation and the stage to which the evaporation of soil and solution is carried.

All the results from various sources for different soils contributed to this study of lime requirement methods emphasize the fact that the Hutchinson-MacLennan method and the McIntire method, as well as all others proposed, are empirical in nature and that comparatively slight variations in procedure affect the results markedly. Results obtained by C. J. Schollenberger with the McIntire method show that this method is quite sensitive in this respect. This is true of methods in which the soil is in contact with solution of calcium hydroxid, carbonate, or solid calcium carbonate and water, as it is of methods which employ a salt solution. If another salt is substituted, the concentration of the solution, or the condition of the soil and the proportion of soil to solution, be changed, different results will be obtained.

Whatever may be the phenomena which gives rise to the so-called acid condition of soil, it can scarcely be expected that any laboratory method will give an indication of the amount of lime which from an economic point of view will be practical for field conditions, for the reason that the reactions between the lime applied to the soil in practice will not take place under the same conditions or to the same extent as when the soil is prepared for the analytical procedure involved.

While methods suggested for the determination of lime requirement are of value in studying the processes which are taking place in the soil, they can not give other than an approximate measure of the soil's need

of bases, which is generally indicated in the case of soils deficient in calcium and magnesium carbonates.

It does not seem advisable that any method for lime requirement or soil acidity be adopted and included in the official methods of the association.

RECOMMENDATIONS.

It is recommended—

(1) That the following modification of the Marr[1] method be adopted as provisional for determination of inorganic carbon in soils:

Place from 5 to 20 grams of soil, depending upon the carbonate content as indicated by a qualitative examination, in a suitable flask or bottle having a capacity of 250 cc. and which will withstand a vacuum of approximately 70 cm. Add 80 cc. carbon-dioxid-free water; after mixing thoroughly connect flask to suitable apparatus[2] provided with condenser and Meyer absorption tube. Start suction, and when air has been removed from apparatus add to the contents of flask, through separatory funnel, 20 cc. dilute hydrochloric acid (2 cc. hydrochloric (specific gravity 1.19) to 18 cc. water).[3]

Allow acid to act on soil for from 5 to 15 minutes, continuing suction, before heating contents of flask. Then boil for from 20 to 30 minutes, maintaining a vacuum of 65 to 70 cm. in the boiling flask. Care should be taken that solution in flask is not drawn up into condenser tube. Absorb carbon dioxid evolved in a suitable quantity of from one-third to one-half saturated barium hydroxid solution, contained in a Meyer absorption tube. The barium carbonate after filtering and washing can be determined either volumetrically[4] or gravimetrically. A blank determination must be made under same conditions and correction applied.

(2) That the referee on soils for 1916 study methods for total sulphur in soils. It is suggested that a comparison of the following methods be made: Sodium peroxid fusion; heating soil with magnesium nitrate solution as used for total phosphorus in soils; modification of Eschka's method for sulphur in coal, ignition of soil with mixture of magnesium oxid, sodium carbonate, and ammonium nitrate.

(3) That methods for extracting sulphates from soils be studied.

(4) That methods for the determination of the total constitutents of soils be studied with a view to substituting them for the "strong acid digestion" as outlined under section 5, page 14, U. S. Bureau of Chemistry Bulletin 107 (revised).

[1] J. Agr. Sci., **3**: (2) 155.

[2] Similar to apparatus described in J. Ind. Eng. Chem. **6**: 561, but omitting Camp absorption tower and substituting Meyer absorption tube.

[3] This proportion of hydrochloric plus the 80 cc. of water previously added gives a strength of acid for decomposition of carbonates of 2 to 100. If the nature of the soil is such that a greater strength of acid is considered necessary, an amount of acid can be taken to make the strength of acid used for digesting soil 3 to 100.

[4] J. R. Cain. J. Ind. Eng. Chem., **6**: 465.

LIME REQUIREMENTS OF SOME ACID SOILS.

By S. D. Conner (Agricultural Experiment Station, Lafayette, Ind.).

A large proportion of the soils of the eastern half of the United States are more or less acid. These soils vary in type from sands, silts, and clays low in organic matter to peats with 80% to 90% volatile matter. Lime experiments have been conducted in field or pot tests on several types of acid soils as follows:

EXPERIMENTS.

Soil No. 1, which is a very acid peat, failed to respond in a pot test with corn to an application of calcium carbonate equivalent to 16,000 pounds per acre, while it did respond favorably to an application of 32,000 pounds.

Soil No. 2 is a peat that has not responded profitably to lime treatment when corn was grown. The total increase of corn in a four-year field test was 91 bushels per acre with a fertilizer rich in potash. When 1,000 pounds per acre of CaO was used together with the fertilizer, the increase was 89 bushels per acre. Three thousand pounds of CaO used alone gave in three years a total increase of 13 bushels of corn per acre.

Soil No. 3, which may be classed as a peaty sand, gave in a three-year field test with eight crops, including corn, wheat, oats, and soy beans, a total yield of 46 bushels of grain and beans per acre when fertilizer was used alone. With 2 tons to the acre of ground limestone added to the fertilizer, the total yield was 201 bushels. With 4 tons of limestone, the total yield was 222 bushels, and with 8 tons of limestone added, the yield was 229 bushels.

Soil No. 4 is a loam well supplied with organic matter. Lime has been used on this soil without noticeable effect on general crops. Clover variety work has been conducted on this soil without lime for the last three years with satisfactory results.

No lime experiments have been conducted on clay soil No. 5.

Soil No. 6 is a white silt or silt loam, which responds to lime on all crops tried, both in the field and in pots. It is interesting to note that in pot work with this soil, clover entirely fails to grow on the untreated soil. Ground limestone at the rate of 2 tons to the acre produces good clover. Ground clover chaff in an application one-third as heavy as the limestone has produced an equally good crop of clover, although the soil still remained acid.

Four soil-acidity methods have been compared in making laboratory estimations of the lime required for these soils. The accompanying table gives the results of these tests, using Hopkins's potassium-nitrate method,

Veitch's limewater method, Hutchinson and MacLennan's calcium-bicarbonate method, and Jones's calcium-acetate method.

Results on acidity of various soils.

SOIL	VOLATILE MATTER	$CaCO_3$ NEEDED PER 2,000,000 POUNDS OF SOIL			
		Hopkins method	Veitch method	Hutchinson and MacLennan method	C. H. Jones method
	per cent	*pounds*	*pounds*	*pounds*	*pounds*
No. 1 (peat)	83.5	8,000	96,430	49,600	74,060
No. 2 (peat)	86.2	1,110	49,290	21,600	36,200
No. 3 (black sand)	8.2	3,670	17,350	12,000	14,260
No. 4 (loam)	7.2	320	3,210	5,200	7,130
No. 5 (clay)	3.9	6,170	6,070	6,800	9,330
No. 6 (silt)	3.0	1,110	1,430	2,400	3,020

DISCUSSION OF RESULTS.

It is seen that the Hopkins method gives much lower results than any of the other methods, especially on the soils containing much organic matter. This method possibly gives too low an estimate as an average; but even so, in most cases it is just as near as any other method to the amounts of lime which have given profitable returns by actual tests on the crops.

While the Veitch method doubtless more accurately determines the amount of lime that a soil has the capacity to absorb, it is seen that it is not profitable to add this much lime to soils high in organic matter.

The results of these tests indicate that organic acidity is much less toxic in soils than inorganic acidity.

The Jones calcium-acetate method gives higher results than the calcium-bicarbonate method. If, however, the titration figures of the Jones method were multiplied by the factor 1.35 instead of 1.8 these two methods would give much more accordant results. None of the soil-acidity methods can be used as an exact estimate of the most profitable amount of lime to be added to the soil. It is only when combined with experience and a knowledge of the use of lime as shown in actual field tests that any laboratory method is valuable. In such connection, I believe a soil-acidity estimation is probably the most important single test that can be made in the laboratory to determine the chemical requirements of the soil.

DETERMINATION OF THE LIME REQUIREMENTS OF SOILS BY THE USE OF CALCIUM BICARBONATE.

By L. P. Howard (Agricultural Experiment Station, Kingston, R. I.)

In connection with one of our ecological problems, it became necessary to have a very accurate method for the determination of soil acidity. The method, above all, whether it bore any relation to agricultural practice, tedious or simple in its technic, must satisfy one condition, namely, it must yield a "requirement" independent, within reasonable limits, of the amount of reacting base and the time of the reaction; that is, it must give the maximum base absorption power of the soil.

No method was available that would stand this test, but the opportune appearance of two new methods in the literature was very welcome. In neither case was any data incorporated in the article to show in how far it might be expected to fulfill our requirements, and it was also readily recognized that each might prove entirely satisfactory with a given soil type and the purpose for which it was devised. We decided to give them careful consideration. Both methods made use of a solution of calcium bicarbonate—ideal in its relation to agricultural practice.

HUTCHINSON-MacLENNAN METHOD.

The first to appear was the Hutchinson-MacLennan[1] method, and it will be discussed first. Its essential points are as follows:

Ten to 20 grams of soil are placed in a bottle of 500 to 1,000 cc. capacity, with 200 to 300 cc. of approximately N/50 calcium bicarbonate. The air in the bottle is displaced by carbon dioxid, the bottle tightly stoppered and placed in a shaking machine for three hours. The solution is then filtered, and a portion of the filtrate equal to half the original amount of bicarbonate is titrated with N/10 acid, using methyl orange as the indicator.

TABLE 1.

Relation of the "requirement" to the amount of calcium bicarbonate used.

SOIL	VOLUME CALCIUM BICARBONATE ADDED	CaO PER 2,000,000 POUNDS OF SOIL	
		Soil No. 5	Soil No. 11
grams	*cc.*	*pounds*	*pounds*
10	100	2,745	4,973
10	200	3,672	6,126
10	200	3,745	6,294
10	300	4,177	6,552
10	300	4,095	6,418
10	400	.....	7,067
10	500	.....	7,414

[1] Chem. News, 1914, p. 2854.

A few trials made at this station were sufficient to show that the reaction was complete in three hours and this time was used in the subsequent work.

CONCLUSIONS.

(1) The reaction is complete in three hours.

(2) The requirement varies according to the amount of reacting base in contact with the soil.

(3) With an arbitrary procedure, closely agreeing duplicates are to be had.

McINTIRE METHOD.

The McIntire[1] method, as proposed before the association at the meeting a year ago, in principle is this: Ten grams of soil are treated with 100 cc. of calcium bicarbonate; the solution quickly evaporated to a thin paste. The residual calcium carbonate is then determined by measuring the carbon dioxid, and this amount subtracted from that added represents that absorbed by the soil. The carbonate was completely decomposed by phosphoric acid, with no appreciable decomposition of organic matter; the time of aspiration was 30 minutes—factors asserted in the method and substantiated by us.

The carbon dioxid was measured volumetrically; and of the several methods employed, the limit of error was least by proceeding in the following manner:

The gas was absorbed in the prescribed manner, the carbonate precipitated with neutral barium chlorid; the solution made neutral to phenolphthalein by slowly adding acid; sufficient standard N/20 acid was added to decompose the barium carbonate; the carbon dioxid boiled out; the solution cooled, and the excess acid titrated with N/50 NaOH.

TABLE 2.

Relation of the "requirement" to the amount of calcium bicarbonate added.

SOIL	VOLUME CALCIUM BICARBONATE ADDED	CaO PER 2,000,000 POUNDS OF SOIL		
		Soil No. 30	Soil No. 11	Soil No. 15
grams	*cc.*	*pounds*	*pounds*	*pounds*
10	100	.....	.....	3,528
10	150	10,640	10,724	.....
10	200	12,684	12,555	.....
10	300	17,052	19,328	.....
10	400	20,720	.....	15,624
10	500	24,080	.....	.....
10	800	.....	.....	21,112

[1] Am. Fertilizer, Nov. 28, 1914, **41**: (11) 36; J. Ind. Eng. Chem., 1915, **7**: 864.

DISCUSSION OF RESULTS.

From the above it is seen that the absorption power of the soil for soluble lime is practically unlimited in any amount that could be reasonably employed in a working method.

TABLE 3.

Relation of the "requirement" to the amount of soil used.

SOIL No. 20	VOLUME CALCIUM BICARBONATE ADDED	CaO PER 2,000,000 POUNDS OF SOIL
grams	*cc.*	*pounds*
10	100	3,797
20	100	3,097
10	150	6,205
20	150	3,836

In some correspondence with Mr. McIntire we learned that working with the Tennessee soils a maximum absorption is secured; that is, the addition of a second portion of bicarbonate resulted in no further absorption. With the majority of soils this may hold true, but with ours the procedure is not applicable.

Can we not adopt an arbitrary procedure yielding comparative results?

With fifteen determinations on a given soil with such a procedure, namely, 10 grams soil and 100 cc. bicarbonate, yielding requirement of 2,820, the probable error of a given determination was ± 62.6.

For our work such a procedure would be undesirable; for as the absorption depends on the excess of reagent, then with widely different soils several determinations would be necessary to discover the proper volume of bicarbonate to add in order that, at the end of the reaction, the amount of residual calcium carbonate might be identical in each case. It seems that a bona fide correlation would be impossible without these conditions being met.

On account of the slight solubility of calcium carbonate in carbonated water and the impossibility of adjusting this excess reagent without increasing the volume of solution, thereby increasing the period of contact, a more complete reaction with the silicates and a subsequent condition vastly different from that which we endeavor to create results.

We tried to correct this condition by adopting a volume of 100 cc. bicarbonate as our standard, thus regulating the time of reaction, and by varying the amount of soil taken. It seemed undesirable to use less than 10 grams of soil, and work with this variation resulted in degrees of absorption which were far from comparable.

We tried using purified precipitated calcium carbonate, in a quantity greater than was possible by using a workable volume of the bicarbonate, adding carbon-dioxid water and evaporating. This proved unsatisfac-

tory in spite of the fact that we learned that on the Tenenssee soils the absorption was proven to take place after the deposition of the calcium carbonate, and the reason for adopting the soluble carbonate was simply to secure a more accurate aliquot.

We believe that it is doubtful whether an absolute method can be evolved which is based on the principle of allowing a certain indefinite amount of reacting base to be in contact with the soil at the end of the reaction. We are now working toward this end, to see whether a workable method can be devised so that at the end of the reaction no excess base remains in contact with the soil. We trust that for those who desire a critical method, our experiences with these methods may be of value.

STATUS OF THE PROBLEM OF LIME REQUIREMENT.

By W. H. McIntire (Agricultural Experiment Station, Knoxville, Tenn.).

The study of the intricate problem of soil acidity or lime requirement has now reached a point where it is well to review and definitely classify the work so far accomplished. But more particularly is it desirable that we designate what constitutes soil acidity or lime requirement, and that there be adopted a terminology which will convey a definite and an accepted meaning.

Methods for the determination of soil acidity or lime requirement have originated from various lines of thought, the consideration of feasible technic often being the deciding factor in advancing a procedure. In some of the work upon soil acidity, much has been assumed, and often qualitative absorption reactions have been used as quantitative acidity indications. The interpretation of the results thus obtained is based upon the assumption that relatively insoluble carbonate of lime would be utilized by the soil in amounts chemically equivalent to the amounts of the CO_2-free, water-soluble alkali salts with which a soil might be treated.

The fallacy of such an assumption may easily be shown. First, no close correlation between a soil's reaction with Na_2O and K_2O can be shown, nor can any correlation between CaO and MgO soil reactions be expressed chemically. Again, during a given time, the absorption will vary with the strength of the soluble salt solution. Let us consider for a moment the relation of the activities between soils and $CaCO_3$ and $MgCO_3$, the alkali earths whose properties and reactions we most commonly consider as being comparable. There is a vast difference between the ability of a given soil to react toward one of these carbonates and that which it exhibits toward the other. Many figures could be cited in

proof of the statement, but the following may be given. In eight instances a given soil was treated under field conditions with 32,000 pounds equivalent of $CaCO_3$ per 2,000,000 pounds of soil and checked against CaO, $Ca(OH)_2$, and $CaCO_3$ in chemical equivalence. Without leaching, the $MgCO_3$ had entirely disappeared in eight weeks, while from each of the three forms of lime about 20,000 pounds of $CaCO_3$ remained. Again, treatments of $CaCO_3$ and of $MgCO_3$ in equivalence of 32 tons of CaO per 2,000,000 pounds of soil gave a difference in residual carbonates of 1.67%, or 33,400 pounds on the original soil basis, while equivalent applications of the two carbonates in amounts equivalent to 200,000 pounds of CaO gave 2.82%, or 56,400 pounds more of residual $CaCO_3$ than of $MgCO_3$. These latter data were obtained in lysimeter investigations one year after treatment. Furthermore, a previous excessive treatment of $MgCO_3$ upon an acid soil will inhibit its ability to further effect an immediate decomposition of $CaCO_3$; however, the presence of an excess of $CaCO_3$, after satisfying lime requirement, will not preclude an extensive decomposition of $MgCO_3$ by the then alkaline soil. Again, strange as it may seem, some soils previously treated with both $CaCO_3$ and Na_2CO_3 still possess to a marked degree the ability to decompose $MgCO_3$, when this is added in carbonated-water solution and thrown out in contact with the soil by evaporation. In other words, there is no relation between the soil's reaction toward finely divided $CaCO_3$ and finely divided $MgCO_3$. Excessive, indeed, would have been lime-requirement results if by chance the more soluble precipitated $MgCO_3$ had been used in carbonated-water solution and the results thus obtained computed to terms of CaO, upon the assumption of chemical equivalence in reaction. Such a procedure would, however, have insured in every instance a sufficient lime-requirement indication.

The more recent trend of opinion has been toward the belief that the correct laboratory procedure to follow in determining soil acidity is to utilize the same material which is used in the field. The idea most prevalent seems to be that if correlation be sought between laboratory methods and field requirements, a soil should have an opportunity to combine with the same compound under both laboratory and field conditions. Since it has been shown that CaO and $Ca(OH)_2$ as used in practice quickly change to carbonate, the latter substance becomes the logical one to use in laboratory practice. But, even an agreement upon this point is not sufficiently definite. Not only must the form of lime be constant, but the fineness and purity of the material must be uniform. There is, both in field and in laboratory, an appreciable difference between the extent of the reaction of an acid soil with precipitated $CaCO_3$ and its activity toward finely ground limestone of comparable purity. If an acid soil be evaporated separately with equal amounts of precipitated

chalk and very finely ground limestone, the decomposition of $CaCO_3$ effected by the soil's acidity is greater in the case of the precipitated chalk than in the case of the limestone. However, in field treatment there is a close parallel to be found between the neutralizing activity of $CaCO_3$, formed in the soil from applied burnt lime and from hydrated lime, and that exerted by precipitated chalk. Moreover, in the parallel of the more active precipitated $MgCO_3$, we have data tending to show that, when applied in excessive amounts, the difference in rapidity of decomposition of a "fluffy" precipitate by an acid soil may be quantitatively denoted as being greater than that of the more crystalline precipitated $MgCO_3$. Again, in addition to variations in degree of fineness, precipitated chalk almost invariably carries some hydrates which must be carbonated by carbonated-water treatment, if this material is to be used for quantitative lime-requirement work. There is but one feasible method of insuring universal uniformity of condition in treating soil with $CaCO_3$, and that is to apply the carbonate as a solution in carbonated water. In so far as we are aware, no stress has been placed upon this fact.

For a period of three years the factors influencing the lime requirements of soils have been studied by the Tennessee Agricultural Experiment Station, as an Adams fund project. When the work was begun in 1912, there were, for the determination of lime requirement, but three methods which directed the use of oxid or carbonate of lime, to wit, the Veitch, the Tache, and the Süchting methods. Of these, only the Veitch gave, after treatment as directed, a soil residue which would produce in the laboratory no further lime requirement immediately subsequent to the acidity test. In other words, of the three methods, only the Veitch gave opportunity for maximum decomposition. It seemed safe to assume that methods which will give but partial indication of a maximum possibility will vary in their partial results, with varying laboratory conditions.

The Veitch method was therefore used as a basis of study, with the hope that its technic might be so modified as to eliminate its laborious features and to render it both rapid and accurate. The laboratory investigations were supplemented by the use of 440 baskets containing three distinct soil types. After trying various modification schemes we found it impracticable to modify the Veitch method for quantitative estimations. We found, however, that upon taking up with distilled water after evaporation, the soil mixture could be agitated and thrown immediately upon a 10-cm. Büchner funnel, thereby securing quickly a clearer filtrate than the supernatant solution to be had after standing overnight. An effort was then made to secure a procedure which would fulfill the requirements of the Veitch method and serve as a

substitute for it. It must be borne in mind that in such a study a certain conception of lime requirement must be held. Upon this point, however, there appears to be no unanimity of opinion. There is no official, provisionally accepted, or adopted definition of the term "soil acidity" or "lime requirement." Hence, it was necessary first to assume certain conditions and to evolve a method which would meet these conditions. The assumption followed was that the lime requirement of a soil may be designated as its ability to decompose a maximum amount of $CaCO_3$ under laboratory conditions, without the decomposition of any neutral organic matter. Such a hypothesis is in harmony with that tacitly assumed in the Veitch procedure. As before stated, from such a study it was found that the only uniform quantitative procedure dependent upon the estimation of residual carbonates by CO_2 determinations involved the use of a $CaCO_3$ solution. Evaporation of soil and $CaCO_3$ effected a greater decomposition of $CaCO_3$ than did boiling for a 5-minute period, and apparently resulted in no decomposition of neutral organic matter. The contact of a partially saturated carbonated solution and soil need be of but brief duration, and no secondary hydrolysis of native minerals is then effected, because of the evaporation which expels the gaseous CO_2. Conditions fulfilling those of the Veitch method were thus met.

The work was carried beyond this point, however, and it was found that after more than satisfying the lime requirement according to the Veitch procedure, unleached and sterile soils were still able to effect, by ordinary contact, continued and appreciable decompositions of $CaCO_3$ with fixation of CaO, principally in the form of silicates. This is in harmony with the work of Veitch, Gardner and Brown, and Hutchinson and MacLennan, who showed that the satisfaction of a soil's original lime requirement, according to indications of the Veitch procedure, does not preclude an additional lime requirement upon unleached potted soils. Elimination of the question of organic matter and biological factors established the fact that the continued decomposition of $CaCO_3$ must be due either to belated reactions of certain less active acid silicates or to hydrated SiO_2, or to a combination of the two causes.

Thus we were led to the conclusion that, speaking chemically, it is necessary to differentiate between what might be termed *temporary*, *immediate*, or *apparent* laboratory lime requirement and *continued* lime requirement of soils.

Contrary to some beliefs, in the rare cases in practice where excess of lime is applied, any excess does not remain inert, save for the loss through leaching, interchange with bases, neutralization of nitric and possibly other acids. In other words, where a soil contains an excess of $CaCO_3$, the excess is diminished gradually, not alone by neutralization, leaching,

and replacement of alkalis, but also by a continued reaction not only with silicates but also with hydrated SiO_2 and TiO_2. The combined influence of these several factors upon the aggregate residual CaO derived from applied $CaCO_3$ has been shown to be of considerable importance in practice. Analyses of the twelve limed plats of the Pennsylvania Agricultural Experiment Station after 32 years of liming showed that of the residual CaO above that of the check plats, about 35% is to be found in silicate combinations. The soil of the check plots, today but slightly acid, and in some cases either neutral or alkaline, has, therefore, accomplished an extensive decomposition of $CaCO_3$ and the fixation of the lime in the soil in combination with silicic acid. This brings us to the consideration of the practical value of a lime requirement determination, and to the point of emphasizing the need of some fixed standard to be met by such a determination. By lime requirement, do we mean a soil's partial or its maximum ability to fix CaO through decomposition of applied lime compounds in the laboratory alone, or do we intend that the laboratory practice shall approach at least a correlation to crop response under field practice? Is it our aim to use a method to determine the laboratory condition of a soil, or to secure data which will afford an indication of its actual or approximate field needs? Would not the latter involve extensive field work over a period of years? Certainly pot or basket work is not sufficient in scope to be altogether conclusive.

It is our belief that in selecting a method for the determination of such an indefinite and elusive soil property as lime requirement, there is need for research, rather than mere comparisons of methods. In coöperative work upon soil problems such as acidity, the referee is confronted with difficulties which do not hinder the referee upon those subjects where various proposed methods may be compared as to their accuracy upon synthetic solutions. *Where there is no unanimity of opinion upon what actually constitutes a desired reaction, he is at a loss to decide when conditions sought are attained,* or which of two or more sets of results may be correct. While affording opportunity for extensive comparisons between methods, our referee system permits of no research to establish the authenticity of results obtained, so far as soils are concerned. Quite naturally, this results in a tendency to lean toward a procedure which offers easy or attractive technic. A case in point is the study of the two methods of lime requirement during the current year. From a research of the factors governing soil acidity, we know that one gives an alkaline condition to the soil residues when these are treated in blank according to the Veitch procedure, while the other falls short of the Veitch requirement, and its residue will give a further lime requirement by duplication of its *own procedure,* or by following any one of four other methods. One represents a maximum reaction, the other a partial one, and one dependent

upon and varying with the amount of charge. But, which indication is correct, the partial or the complete? What is the viewpoint to be assumed, that of the laboratory or that of the field? If field applications be taken as the viewpoint, how are we to know which procedure may be preferable? It is quite possible that two methods would give indications which might give closely concordant increases in yields for the first year, but after that, returns which might indicate the advisability of the larger indication. Furthermore, recent work at the Iowa Agricultural Experiment Station has shown that fineness of division of the sample taken for analyses is an important consideration. That is, a soil, acid when coarsely ground, may become alkaline to Veitch tests when more finely ground. More recently the reverse has also been shown to be possible. What, then should be the fineness of the analyzed sample?

This association has shown its appreciation of the importance of the phosphate question by appointing a very able committee to study this problem. It will be readily conceded that in many cases liming is a prerequisite to the profitable use of acid phosphate as well as other fertilizers and that the subject of lime is, therefore, of equal importance to that of phosphate availability. Would it not, therefore, be in line of conservative yet progressive accomplishment for this association to designate a committee of its members to definitely determine what shall be officially considered as constituting lime requirement, to decide upon a definite degree of fineness, and to further decide whether it be advisable for this association to attempt a correlation between laboratory procedure and field practice, or whether the laboratory problem alone shall be solved, leaving the field problem of the variable factors of crop and influence of soil type and climatic conditions to such an organization as the American Society of Agronomy?

In the treatment of the lime-requirement problem, such questions could and would be carefully considered and settled, were this association to adopt toward it a policy similar to its method of handling the phosphate problem. But at least, let us cease to evade the issue; let us be agreed as to what constitutes immediate, temporary, or apparent soil acidity and adopt for such some definite terminology.

DETERMINATION OF PHOSPHORUS IN SOILS.

By H. A. Noyes (Agricultural Experiment Station, Lafayette, Ind.).

Due to evidence presented by Hilgard,[1] Goss,[2] and others, it is well established that strong acids will dissolve the phosphorus present in soils.

[1] U. S. Dept. Agr., Div. Chem. Bul. 38.
[2] U. S. Dept. Agr., Div. Chem. Bul. 43.

Since the method of Goss dissolves the phosphorus and requires less time to prepare a solution for analysis, it has been used in all investigational work conducted by the author of this paper. With clay soils, subsoils, and some freak soils difficulty is experienced in dissolving with nitric acid the precipitate formed on preliminary neutralization of the prepared solutions. It has also been observed that those samples where it is hard to dissolve the ammonium hydroxid precipitate are the ones where later on in the procedure the yellow precipitate is hard to dissolve and where clean, clear solutions are not present when the phosphorus is reprecipitated as magnesium ammonium phosphate.

Sulphuric acid is a weaker acid than nitric acid. This leads us to believe that if a proper amount of ammonium nitrate was added to the original aliquot there would be no loss of phosphorus due to increased solubility of ammonium phosphomolybdate.

When the laws of physical and chemical equilibrium are applied to solutions that have and have not been neutralized before precipitation of ammonium phosphomolybdate we find the same possibilities of ionic concentration, molecular combination, and solubility. This is true if ammonium nitrate is added to the solutions. That the positive H ions in the solution in either case are offset principally by negative NO_3 ions is borne out by the fact that nitric is a stronger acid than sulphuric and ammonium sulphate is less soluble than ammonium nitrate.

The P_2O_5 results given in the following table were obtained on 10 soils chosen for their variation in acid oxidizable material. The method of analysis is that of Goss,[1] except that for every 25 cc. aliquot of solution taken 15 grams of dry ammonium nitrate is added at the outset to the set of solutions that received no preliminary neutralization.

Soil analysis—dry basis.

SOIL	P_2O_5 NEUTRALIZED	P_2O_5 UNNEUTRALIZED	INORGANIC CO_2	ORGANIC C	N
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Iron soil	1.51	1.50	0.068	4.38	0.64
Do	*2.45	2.41	0.018	0.75	0.13
Black soil	0.53	0.53	0.033	18.63	2.41
Acid peat	0.44	0.45	0.002	23.88	2.16
Black sand	0.41	0.43	0.018	2.16	0.38
York silt loam	0.12	0.13	0.000	0.51	0.02
Gumbo	0.47	0.48	0.230	1.77	0.41
Hog loam	0.34	0.34	0.101	0.95	0.16
Red sand	*0.16	0.15	0.000	0.38	0.05
Decatur clay loam	*0.17	0.15	0.030	0.59	0.09

The results indicated by an asterisk (*) in the table denote those solutions which on neutralization with ammonia did not give precipitates

[1] Wiley. Principles and Practice of Agricultural Analysis, vol. 1, p. 465.

that were readily redissolved by nitric acid and which subsequently gave slightly cloudy solutions on standing with the magnesium ammonium phosphate precipitate.

CONCLUSION.

Nothing is gained by the neutralization of the phosphorus solution with ammonia and subsequent dissolving of precipitate with nitric acid before precipitation of ammonium phosphomolybdate. Neutralization may precipitate substances from the original solution that are not easily redissolved after being precipitated.

STUDY OF SOIL CONTAINING RESIDUAL LIMESTONE.

By H. A. Noyes (Agricultural Experiment Station, Lafayette, Ind.).

In connection with an Adams-fund project on orchard management, under investigation in the horticultural department, the acidity of the soil at different depths was studied. The soil is a residual silty clay containing about 60% very fine silt and 20% clay, underlain with limestone rock. Samples were taken representing the following depths: 0 to 9 inches, 9 to 18 inches, 18 to 27 inches, 27 to 36 inches, and 36 to 45 inches, where no bed rock was found above the 45-inch depth.

The samples representing the different depths were air-dried, fined with a wooden rolling pin, and sieved through a 40-mesh sieve. Limestone fragments varying in size from that of a kernel of wheat to 2 cm. in diameter were found in eight samples representing three of the places chosen for sampling. The following table gives the results of determinations made on the samples taken at these three places. Stress is not laid on the amount of acidity, nor on the accuracy of the method employed for determining acidity, but on the fact that this standard method places the soil as acid. The acidity, determined by the Hopkins potassium-nitrate method, is expressed as pounds of calcium carbonate necessary to neutralize 9-inch layers (3,000,000 pounds) of this soil. The column headed calcium carbonate reports the acid neutralizing powers of the limestone particles where found in the soil as percentage purity of calcium carbonate. Columns headed hygroscopic moisture, volatile matter, and nitrogen are given as per cent of air-dry soil.

Determinations on residual limestone soils.

SAMPLE NO.	DEPTH	ACIDITY EQUIVALENT $CaCO_3$	PURITY LIMESTONE FRAGMENTS	HYGROSCOPIC MOISTURE	VOLATILE MATTER	NITROGEN
	inches	*pounds*	*per cent*	*per cent*	*per cent*	*per cent*
X–28	0 to 9	112.5	.....	1.96	4.39	0.12
	9 to 18	919.9	.....	2.50	4.74	0.11
	18 to 27	787.5	.....	(1)	(1)	(1)
	27 to 36	30.0	.....	(1)	(1)	(1)
	36 to 41	(2)	93.8	3.85	6.13	0.06
XI–23	0 to 9	1,087.5	.....	3.31	4.75	0.10
	9 to 18	187.5	.....	3.66	5.43	0.09
	18 to 27	37.5	73.8	2.70	6.94	0.06
	27 to 36	56.4	89.9	2.73	6.46	0.06
	36 to 45	150.0	89.0	3.80	5.52	0.07
III–51	0 to 9	112.5	.....	2.04	6.49	0.21
	9 to 18	(2)	94.3	2.63	5.75	0.13
	18 to 27	56.4	96.3	2.97	5.43	0.10
	27 to 36	75.0	90.4	2.40	7.77	0.11
	36 to 40	18.9	83.5	2.27	8.68	0.05

[1] Not determined.
[2] Sweet.

DISCUSSION.

The acidity does not decrease the deeper we go down into the soil. In all three places reported upon here, as well as in the other places investigated, the acidity shows no regular decrease or increase dependent upon the distance from bed rock. The acidity results can not be correlated either with the percentage of nitrogen or volatile matter in the samples. The volatile-matter figures probably are governed more by variations in combined water than by actual organic-matter content.

The state of fineness of limestone for agricultural use in correcting soil acidity has been a subject of both experimentation and comment. In the 1912–13 report of the Pennsylvania Agricultural College, page 214, we note the following: "We conclude, therefore, that on silty loams and on soils of heavier texture, on lands where soil acidity is the chief factor limiting clover production, crushed limestone used for amendment should be at least 60-mesh in fineness of pulverization." This statement is based on experimental results using limestone of varying fineness and clover as the indicator of its effect in correcting acidity.

The presence of limestone fragments in the residual acid soil reported upon here points to the conclusion that coarse screenings would not correct the acidity.

The Pennsylvania report shows results of lime when it is applied experimentally. The soil reported on here has coarse particles of limestone left from nature's original supply, and yet it is acid.

It is taken for granted that acid loams, silts, and clays, of which there are large areas, need clover and that clover responds better on a soil neutral or alkaline in reaction. In conclusion, silt and clay soils need finely ground limestone and not coarse screenings to correct soil acidity.

REPORT ON INORGANIC PLANT CONSTITUENTS.

By A. J. Patten (Agricultural Experiment Station, East Lansing, Mich.), *Referee.*

In presenting a report on this subject, I wish to briefly review the work carried on during the past four or five years, in so far as it relates to the discussion which follows.

In 1910 the molybdate method for the separation of ferric and aluminic oxids was studied. This method provides for the removal of the phosphoric acid by precipitating with the usual molybdate solution, and the precipitation of the iron and aluminum in the filtrate, by cautiously making it ammoniacal, keeping the temperature below 40°C. For this work a synthetic solution containing 30% CaO, 10% MgO, 2% Fe_2O_3, 3.98% Al_2O_3, and 9.70% P_2O_5 was used.

In 1911, on a solution containing 23% CaO, 10% MgO, 3% Fe_2O_3, 2% Al_2O_3, and 16.81% P_2O_5, the molybdate method was again studied, and in addition the oxalate method for the separation of ferric and aluminic oxids. Some results were also reported by the referee on an extension of the molybdate method to include calcium and magnesium.

In 1912 the same methods were again studied, but no results were reported. However, the molybdate method for the separation of ferric and aluminic oxids was made official, and it was recommended that further work on the oxalate method be discontinued and that the molybdate method, extended to include calcium and magnesium, be further studied.

In 1913 on a solution containing 11.38% CaO and 9.30% MgO the extended molybdate method was further studied and the following recommendation was made:

> That the official method for iron and aluminum be extended to include calcium and magnesium in the presence of minute quantities of manganese.

No report was presented in 1914, and the same recommendation was referred to the present referee. The work carried on during the past year has, therefore, been confined to a study of methods for the determination of calcium and magnesium. The reasons advanced for extending the molybdate method to include calcium and magnesium may, perhaps,

be best expressed by quoting from the report of a former referee, under whose direction most of the work has been carried on.

> It is not the intention of the referee to have the new scheme of analysis take the place of the present one, but rather to supplement it, if after it has been tested by the association it is found satisfactory, as there is no doubt that there will be much time and work saved by using it. The method will have another advantage in that the phosphoric acid, ferric and aluminic oxids, calcium and magnesium oxids, and possibly the manganese can be estimated in the same solution on one-half gram of ash, which is very desirable when the sample is small. Still another advantage which might be mentioned in its favor consists in avoiding the acetate separation, which at best is not very satisfactory in the hands of the average analyst.

On reviewing the results reported in previous years for calcium and magnesium by this method, they are found, in most instances, to be very satisfactory except where manganese was present in the ash solution. In such cases the calcium precipitate was always contaminated with manganese, which, where the amount was determined, was found to vary from 0.3 to 2 mg. Mn_3O_4.

Comparisons have been made in the referee's laboratory between the official and molybdate methods for the determination of calcium and magnesium in solutions approximately the same as those used in other years. The results were practically the same by both methods, except that manganese, when present, was invariably occluded by the calcium precipitate in the molybdate method. The amount was small, however, in every case amounting to less than 4% of the total weight of the calcium oxid. The presence of manganese is plainly visible after ignition, on account of the color imparted to the calcium oxid, and because of this fact the error often appears much greater than is actually the case. The official method provides for the removal of the manganese before the precipitation of calcium, and it is consequently not a source of error in the latter determination.

Another disadvantage in the molybdate method is the time required to complete the determinations, and when only calcium and magnesium are to be determined the time factor is a serious drawback. However, in defense of the molybdate method it should be stated that when phosphoric acid, iron, and aluminum are also to be determined the time factor is no longer an objection. Since all of the previous work on the extension of the molybdate method to include calcium and magnesium has been done on synthetic solutions, it will be of interest to compare them with the ash of a variety of plant materials as given in the following table. No figures were available for ferric and aluminic oxids, but it is fair to assume that they would in every case be less than that for calcium oxid.

Composition of the ash of plants.

PLANT	K_2O	Na_2O	CaO	MgO	P_2O_5
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Seeds of cereals:					
Wheat	31.0	2.0	3.3	12.0	47.3
Barley	21.3	2.4	2.6	8.7	34.7
Oats	17.8	1.6	3.5	7.1	25.5
Corn	29.5	0.9	2.7	15.5	45.5
Seeds of legumes:					
Soy bean	42.4	0.9	5.5	8.3	36.9
Pea	43.8	0.5	4.9	8.8	36.0
Red clover	35.6	1.1	6.6	13.2	38.0
Garden bean	41.9	1.0	5.0	7.2	39.3
Straw:					
Wheat	13.7	1.4	5.8	2.5	4.9
Barley	23.3	3.5	7.2	2.7	4.2
Oats	26.4	3.3	7.0	3.7	4.6
Corn	30.1	1.2	10.8	5.6	8.1
Bean	43.2	1.7	26.6	5.8	6.4
Hay:					
Meadow hay	25.1	4.5	15.8	7.1	6.1
Red clover	32.3	2.0	34.9	10.9	9.7
Alfalfa	31.4	2.4	31.4	7.8	5.8
Roots and tubers:					
Potato	60.2	3.0	2.7	5.0	16.9
Turnip	50.0	7.8	11.7	2.6	10.3
Sugar beet	53.3	8.9	6.1	7.8	12.2
Mangel	52.3	16.3	3.7	4.3	8.7
Synthetic solutions:					
1910	20.0	0.8	30.0	10.0	9.7
1911	40.0	3.0	23.0	10.0	16.8
1913	.....	.....	11.4	9.3	.....

On examining this table we find that the composition of the ash of the several materials varies within very wide limits. The ash from seeds invariably contains very large amounts of phosphoric acid and small amounts of calcium and magnesium, the latter being two to four times that of calcium, while the ash from straws contains small amounts of all three of these constitutents. In the ash from meadow hay, red clover, and alfalfa, the percentage of calcium is considerably more than that of phosphoric acid or magnesium, and the ash from roots and tubers contains somewhat more phosphoric acid than calcium or magnesium, but in no case does the phosphoric acid content approximate that in the ash from seeds.

The composition of the synthetic solutions used in 1910 corresponds very closely to the ash of red clover hay, but the solutions used in 1911 and 1912 are quite different, and none of them resemble in any respect the ash from seeds, straws, or roots.

From the evidence here presented, it is evident that the determination of iron, aluminum, calcium, and magnesium in the ash from wheat grain presents quite a different problem from the determination of the same constituents in the ash from wheat straw and other coarse fodders. In

the latter case either or both of the methods under discussion should give good results, while in the former case neither of them are applicable. For example, in attempting to determine the calcium by the molybdate method in an ash solution from wheat grain, if an aliquot corresponding to 1 gram of ash and equivalent to only 33 mg. CaO were taken, it would be necessary to use no less than 500 cc. of molybdate solution to precipitate all of the phosphoric acid. On the other hand, if an aliquot representing one-tenth gram of ash were taken, so as to reduce the phosphoric acid to an amount more nearly normal, then the amount of calcium oxid (3.3 mg.) would be so small as to render its accurate determination, under such conditions, almost if not quite impossible. The same would, likewise, be true of the other constituents, and for similar reasons the official method for calcium and magnesium cannot be depended upon with solutions high in phosphoric acid.

No collaborative work has been asked for this year, but what time the referee has been able to devote to the subject has been along the line of developing a method for calcium and magnesium that would be applicable to the ash of seeds as well as coarse fodders. In this connection, both Meade's[1] and McCrudden's[2] methods, which provide for the precipitation of calcium in the presence of phosphoric acid and iron, have been studied. From the work already done it is believed that one or the other of these methods may be adapted not only for the determination of calcium but also magnesium, iron, and aluminum without removing the phosphoric acid. Some progress has been made along this line, but it was not considered advisable to report that part of the work this year.

RECOMMENDATIONS.

It is recommended—

(1) That the present official methods for iron, aluminum, calcium, and magnesium be made official only for plant materials other than seeds.

(2) That the extension of the official method for iron and aluminum, as recommended by the referee in 1913, be made a provisional method for calcium and magnesium in the presence of minute quantities of manganese for plant materials other than seeds.

(3) That suitable methods be devised for the determination of iron, aluminum, calcium, and magnesium in the ash from seeds.

[1] Chem. Eng. 1–21; also Meade's Portland Cement, p. 189.
[2] J. Biol. Chem., **7**: 83.

REPORT ON INSECTICIDES.

By R. C. Roark (Bureau of Chemistry, Washington, D. C.), *Referee.*

The coöperative work on insecticides for 1915 has been a study of methods for the determination of the most important ingredients of the following insecticides and fungicides: Paris green, lead arsenate, lead arsenate with lead arsenite, calcium arsenate, zinc arsenite, nicotin solution, Bordeaux mixture, Bordeaux-Paris green, Bordeaux-lead arsenate.

Some of these methods were tested last year, while others are being considered for the first time this year.

Twenty-six laboratories were invited to coöperate in the work. Of these, 13 promised to assist in some part of the work, and results have been received from 15 analysts in 10 different laboratories. In addition, 6 chemists in the Insecticide and Fungicide Laboratory of the Bureau of Chemistry have assisted the referee, making a total of 22 coöperators.

PARIS GREEN.

The methods tested are the following:

TOTAL ARSENIC.

METHOD I.

(Method of Thorn Smith, modified.)

Solutions required.—Prepare starch solution, standard arsenic trioxid solution and standard iodin solution as directed in Journal of Industrial and Engineering Chemistry, volume 8 (1916), page 330; also Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 5, paragraph 3.

Determination.—Weigh carefully an amount of Paris green such that when decomposed and made up to volume in a graduated flask 50 cc. of the solution will contain an amount of Paris green equal to the amount of arsenious oxid to which 100 cc. of the iodin solution are equivalent. (Example: If 1 cc. of the standard iodin solution = 0.002841 gram As_2O_3, weigh $5 \times 0.2841 = 1.4205$ grams Paris green, and when decomposed make up to volume in a 250 cc. flask). Transfer the Paris green to the graduated flask by means of about 100 cc. of a 2% sodium hydroxid solution, and boil the mixture thoroughly until no green particles are visible. Cool and make up to volume. Filter the well-shaken liquid through a dry filter and use 50 cc., portions for analysis. Pipette 50 cc. into an Erlenmeyer flask, dilute to about 100 cc. with water, add 3 to 4 cc. of concentrated sulphuric acid and 1 gram of potassium iodid, and boil down to 40 cc. Cool under running water, and add approximately N/20 thiosulphate solution drop by drop from a burette until the solution is exactly colorless. Add sodium bicarbonate in excess and titrate with the standard iodin solution as directed under "Standardization." The number of cubic centimeters of iodin solution used in this titration represents directly the total per cent of arsenic in the sample, expressed as As_2O_3. (If any arsenic should be present in the form of arsenate, it will be titrated as As_2O_3 according to this method).

METHOD II.

(Distillation method of Roark and McDonnell.)

Proceed as directed in Journal of Industrial and Engineering Chemistry, volume 8 (1916), page 330; also Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, pages 5–6, paragraphs 4–5.

METHOD III.

Total arsenic present as As_2O_3 only.

(a) *Procedure of C. C. Hedges, modified.*—Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, pages 6–7, paragraphs 6–7.

(b) *Procedure of C. M. Smith, modified.*—Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 7, paragraph 8.

Analyses of Paris green.

ANALYST	TOTAL ARSENIC AS As_2O_3			
	METHOD I	METHOD II	METHOD III (a)	METHOD III (b)
	per cent	*per cent*	*per cent*	*per cent*
C. H. Robinson, Ottawa, Canada	57.65	57.00	56.10	56.85
	57.80	56.75	56.25	56.80
	57.75	56.75	56.30	56.80
	57.70	.....	.....	.....
Average	57.72	56.83	56.20	56.81
Hugh L. Fulmer, Guelph, Canada	57.05	56.90	56.90	57.20
	56.90	56.90	57.00	57.30
Average	56.98	56.90	56.95	57.25
A. C. Whittier, Newark, Del	57.30	56.60	57.50	57.20
	57.40	56.50	57.30	57.30
	57.10	56.60	57.30	57.20
Average	57.27	56.57	57.37	57.23
W. L. Latshaw and J. C. Ripperton, Manhattan, Kans	.....	56.90	.....	.....
	.....	56.90	.....	.....
Average	.....	56.90	.....	.....
A. J. Flume, Geneva, N. Y	56.60	57.18	56.60	56.65
	56.60	57.26	56.55	56.70
	.....	56.55	56.65	.....
Average	56.60	57.00	56.60	56.68
A. L. Sherman, Pullman, Wash	57.72	.....	57.04	57.04
	57.50	.....	.....	57.09
	57.83	.....	.....	.....
Average	57.68	.....	57.04	57.07

Analyses of Paris green—Continued.

ANALYST	TOTAL ARSENIC AS As_2O_3			
	METHOD I	METHOD II	METHOD III (a)	METHOD III (b)
	per cent	*per cent*	*per cent*	*per cent*
F. L. Elliott, Washington, D. C.	56.75	57.00	57.00	57.00
	56.75	56.80	57.00	57.05
	56.70	.....	56.90	56.95
Average	56.73	56.90	56.97	57.00
J. J. T. Graham, Washington, D. C.	56.60	56.65	57.10	57.10
	56.85	56.70	57.05	57.10
	56.60	.....	57.05	57.15
	56.75	.....	.....	.....
Average	56.70	56.68	57.07	57.12
W. J. Morgan, Washington, D. C.	.....	57.20	57.10	57.20
	.....	57.20	57.10	57.20
Average	.....	57.20	57.10	57.20
E. J. Nealon, Washington, D. C.	.....	56.90	.....	57.15
	.....	57.00	.....	57.20
Average	.....	56.95	.....	57.18
C. H. Walker, Washington, D. C.	56.56	56.25	56.29	56.63
	56.56	56.15	56.63	56.58
	.....	.....	56.05	.....
	.....	.....	56.34	.....
Average	56.56	56.20	56.33	56.61
R. C. Roark, Washington, D. C.	56.80	57.10	57.15	57.20
	57.00	57.10	57.20	57.20
	56.90	.....	57.15	57.15
Average	56.90	57.10	57.17	57.18
George E. Holm, St. Paul, Minn.	56.02	56.40	55.41	55.60
	56.10	56.45	55.38	55.57
	56.24	.....	.....	.....
Average	56.12	56.43	55.40	55.59
W. H. Rogers and E. R. Tobey, Orono, Me.	57.60	57.30	57.90	57.60
	57.30	57.50	57.80	57.40
	57.60	.....	57.80	.....
Average	57.50	57.40	57.83	57.50
General average	57.00	56.84	56.84	56.97

COMMENTS BY COÖPERATORS.

A. L. Sherman (commenting on Method I): The addition of sodium thiosulphate did not determine the end point decisively enough, hence a drop of starch was used as an indicator. If the solution could be diluted before adding thiosulphate the

end point would be easier to see. (He found that in Method III (a) no heat was required to dissolve the sample.)

Hugh L. Fulmer: I have no particular criticism to offer in respect to any of the above methods, except in the determinations where potassium iodid is used. Where this substance is used, particularly in the analyses of Paris green, I found it very difficult to decolorize with sodium thiosulphate except by using a large excess of this solution, a great deal more than was required to actually destroy the free iodin present. If I added enough sodium thiosulphate for complete decolorization, as near as I could judge, the end point being very indefinite, I obtained the following results with Paris green: (1) 65.7% As_2O_3; (2) 69.3% As_2O_3. Results, as you see, are very unsatisfactory, being 8% to 12% above the correct quantity, showing of course that a large excess of sodium thiosulphate had been used to bring about complete decolorization. I therefore adopted the method of using a starch indicator when adding sodium thiosulphate to remove the excess of free iodin.

A. J. Flume (in regard to the distillation method for arsenic): In no instance did the flask containing sodium bicarbonate and water show the presence of arsenic.

DISCUSSION.

The referee, in the course of the analysis of a great number of different arsenicals by the distillation method, has never observed the presence of arsenic in the third flask either, but feels that it is a wise precaution to have a third flask in the series to catch the acid distillate. As the method is presented in this report, the sodium bicarbonate has been omitted from the third flask, and the directions call for mixing the contents of all three flasks instead of testing the third one separately, which was directed to be done in the first set of directions sent out.

The referee regards the distillation method for arsenic, as described in this report, as by far the most accurate of any. A distillation may be made in 30 to 35 minutes, and if a battery of condensers is available, a number of distillations may be made at one time. After dilution, the distillate may be kept in a stoppered flask indefinitely without loss of arsenic.

This method is particularly valuable in that it determines arsenic in both the "ous" and "ic" forms and at the same time effects a separation from antimony. The presence of antimony in arsenical insecticides has never been noted heretofore, but lately in this laboratory it has been shown to be present in zinc arsenite, and there is reason to believe it occurs in small amount in many other insecticides.

Method I is a modification of the present official method (U. S. Bur. Chem. Bul. 107 (rev.), pp. 25–26) which is the method of Thorn Smith (J. Am. Chem. Soc. 1899, **21**: 769–772). As modified, the method is simplified and rendered easier of manipulation and in the calculation of results. However, it is not as accurate nor even as quick as the distillation method, and the referee believes, therefore, that it should be discarded in favor of the distillation method. In regard to the modified methods of

Results on various Paris greens.

LABORATORY NO.	TOTAL ARSENIC AS As_2O_3			LABORATORY NO.	TOTAL ARSENIC AS As_2O_3		
	Thorn Smith original method	Method II (Distillation)	Method III (b)		Thorn Smith original method	Method II (Distillation)	Method III (b)
	per cent	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*
12312	55.70	55.60	56.55	12481	55.90	56.40	56.20
	55.60	55.60	56.50		56.08	56.30	56.20
	.....	.....	56.50		.....	.....	56.25
Average	55.65	55.60	56.52	Average	55.99	56.35	56.21
12314	56.43	55.90	56.70	12483	57.26	56.90	57.10
	56.40	55.80	56.70		57.07	56.90	57.10
	.....	.....	56.75		.....	.....	57.00
Average	56.42	55.85	56.72	Average	57.17	56.90	57.07
12402	56.86	56.70	57.20	12486	61.65	61.90	61.60
	56.76	56.70	57.10		61.53	62.10	61.70
	.....	.....	57.10				
Average	56.81	56.70	57.13	Average	61.59	62.00	61.65
12404	56.50	56.60	57.20	12488	58.34	58.20	58.10
	56.50	56.60	57.00		58.22	58.25	57.90
	.....	.....	57.10				
Average	56.50	56.60	57.10	Average	58.28	58.23	58.00
12474	55.04	55.50	55.60	12489	56.51	56.85	57.15
	55.18	55.45	55.80		56.45	57.00	57.15
	.....	.....	55.80				
Average	55.11	55.48	55.73	Average	56.48	56.93	57.15
12477	56.89	57.20	57.00	12542	56.79	57.20	57.40
	57.01	57.20	57.30		56.86	57.20	57.30
	.....	.....	57.30		.....	.....	57.10
Average	56.95	57.20	57.20	Average	56.83	57.20	57.27
12478	56.76	57.30	57.05	12544	55.77	55.35	56.50
	56.66	57.30	57.20		55.71	55.30	56.60
	.....	.....	57.25		.....	.....	56.60
Average	56.71	57.30	57.17	Average	55.74	55.33	56.57
12480	57.01	57.05	56.65	12782	55.29	56.00	55.40
	57.20	57.00	56.65		55.21	56.00	55.40
	.....	.....	56.60		.....	.....	55.55
Average	57.11	57.03	56.63	Average	55.25	56.00	55.45
				12783	55.97	56.65	56.45
					55.91	56.70	56.50
					.....	.....	56.35
				Average	55.94	56.68	56.43

Hedges and C. M. Smith, these are very quick methods and are useful in determining the approximte composition of a Paris green, but they have serious limitations. They determine arsenic when present as As_2O_3, but not as As_2O_5; they will determine any antimony present as Sb_2O_3; and they are affected by cuprous and ferrous salts. It is not unusual for a Paris green to contain some arsenic as an arsenate or some copper as a cuprous instead of a cupric salt. The referee believes that these methods should be brought to the attention of the association as quick and useful methods for determining the approximate composition of a Paris green, but they should not be adopted as official.

In the original method of Hedges (J. Ind. Eng. Chem., 1909, **1:** 208) the Paris green was dissolved in 1 to 1 hydrochloric acid at a temperature of not over 80°. No directions are given for getting the copper which is precipitated upon addition of sodium bicarbonate back into solution, although a large excess of that reagent will do it. As modified by the referee, the directions call for making the solution at a lower temperature and in more dilute acid, and ammonium chlorid is used to dissolve the copper precipitate.

The method of Avery and Beans (J. Am. Chem. Soc., 1901, **23:** 485–486) is very similar to that of Hedges in that the sample is dissolved in hydrochloric acid and the arsenic is titrated in the presence of copper, which is held in solution by sodium potassium tartrate. Avery and Beans state that cuprous salts interfere with the titration in their method, and also that results are higher than by other methods. Lander and Geake (Analyst, 1914, **39:** 116–121) confirmed the interference of cuprous salts in this method and found that ferrous salts also rendered the method inaccurate.

The Avery-Beans method was studied by the association in 1901 (U. S. Bur. Chem. Bul. 67, p. 101), in 1902 (U. S. Bur. Chem. Bul. 73, pp. 159–160; U. S. Bur. Chem. Circ. 10, p. 2), and in 1903 (U. S. Bur. Chem. Bul. 81, pp. 196–198) and was found to give erratic results, due to the difficulty in dissolving free arsenious oxid in dilute hydrochloric acid. Modifications of this method were studied also (U. S. Bur. Chem. Bul. 81, pp. 196-198; J. Am. Chem. Soc.1903, **25:** 963–968 and 1096–1097; U. S. Bur. Chem. Bul. 90, pp. 96–99; U. S. Bur. Chem. Bul. 99, pp. 26–27) with the result that those of Avery and Haywood were adopted as optional official methods (U. S. Bur. Chem. Bul. 107 (rev.), pp. 26–27).

The objectious urged against the original Avery-Beans method apply equally to Hedges's method, but not to that of C. M. Smith, for when sulphuric acid is used to dissolve Paris green the solution may be boiled, which will dissolve any free arsenious oxid present without loss by volatilization.

The referee in 1914 recommended that Methods II and III of U. S. Bureau of Chemistry Bulletin 107 (revised), pages 26 and 27, which are the methods of Avery and Haywood above referred to, be discarded, and this was done by Committee A (J. Assoc. Off. Agr. Chem., 1916, 2:43). This recommendation was made because the distillation method is more accurate, and preferable as to manipulation.

The referee believes that the method of Hedges, while as accurate as that of C. M. Smith in the analysis of a pure Paris green, is not of such general applicability, e.g., to a Paris green containing free arsenious oxid, and that the latter method is greatly to be preferred.

In the accompanying table, results on various samples of Paris green obtained on the market, by the present official method, the distillation method, and the method of C. M. Smith (modified) are presented. The figures are not strictly comparable because, according to the official, or Thorn Smith, method, any antimony that might be present would be determined as arsenic; the distillation method determines arsenic only, while Method III (b) determines both arsenic and antimony present in the "ous" but not in the "ic" state. Method III (b) is also affected by cuprous and ferrous salts.

LEAD ARSENATE.

TOTAL ARSENIC.

METHOD I.

(a) Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 10, paragraph 29.

(b) Weigh an amount of the powdered sample equal to twice the amount of arsenic oxid (As_2O_5) to which 100 cc. of the standard iodin solution are equivalent, transfer to a porcelain casserole or evaporating dish, add 5 cc. of concentrated sulphuric acid, and heat on the hot plate to copious evolution of white fumes of sulphuric acid. If the mixture remains black from the presence of organic matter, add a few cubic centimeters of concentrated nitric acid, and repeat the evaporation with concentrated sulphuric acid until all organic matter is destroyed. Cool, add about 50 cc. of water, allow to stand until all the lead sulphate settles quickly to the bottom, then filter. Wash the precipitate on the filter thoroughly with cold water, collecting the filtrate in an Erlenmeyer flask, and proceed as directed under (a) above.

METHOD II.

Total arsenic present as As_2O_5 only.

Starch solution.—Prepare as directed under Paris green.

Standard iodin solution.—Prepare as directed under Paris green, but calculate in terms of As_2O_5. Factor: $As_2O_3 \times 1.16168 = As_2O_5$.

Standard thiosulphate solution.—Prepare an approximately N/20 solution as follows: Weigh 13 grams of crystallized sodium thiosulphate, dissolve in water, and make to 1,000 cc. To standardize this solution proceed as follows: To 25 cc. of concentrated hydrochloric acid and 10 cc. of water in an Erlenmeyer flask add 50 cc. of the standard iodin solution, preferably from a pipette, keeping the contents of

the flask at a temperature of 35° to 40°C., and immediately titrate with the standard thiosulphate solution. When the color of the solution becomes a faint yellow, dilute with about 150 cc. of water, and continue the titration carefully drop by drop until the solution is colorless. It is well to add a little starch paste near the end of the titration to make sure of the end point. The value of the iodin solution in terms of arsenic pentoxid being known, from the ratio of the two solutions calculate the value of the thiosulphate solution in terms of arsenic pentoxid (As_2O_5).

Determination.—Weigh an amount of the powdered sample equal to twice the amount of arsenic pentoxid to which 100 cc. of the thiosulphate solution are equivalent. Transfer to an Erlenmeyer flask, and dissolve in 25 cc. of concentrated hydrochloric acid, warming on the steam bath. When solution is complete, cool to 35° to 40°C., add 10 cc. of potassium-iodid solution (20 grams KI per 100 cc.) and 50 cc. of ammonium-chlorid solution (25 grams NH_4Cl per 100 cc.), and immediately titrate the liberated iodin with the thiosulphate solution as directed above. The number of cubic centimeters of thiosulphate solution used in the titration divided by 2 represents directly the per cent of arsenic pentoxid (As_2O_5) in the sample. (Any arsenic that may be present in the sample in the "ous" form is not determined by this method.)

NOTE.—The following are important points in this method and should be closely followed:

(1) Temperature at which reduction of As_2O_5 takes place. If the KI is added to the hydrochloric-acid solution of the lead arsenate at too high a temperature some iodin is lost by volatilization; if at too low a temperature, the reaction does not proceed to completion. A temperature between 35° and 40°C. should be maintained.

(2) Dilution affects the results markedly. The solution should not be diluted until the color has become a faint yellow, then dilution should be made in order to slow down the liberation of the iodin so that the end point will be stable.

(3) Speed of titration: The titration should be carried out without delay, as on standing more iodin will be liberated.

(4) When dissolving the sample in the concentrated hydrochloric acid by warming on the steam bath, the solution must not be allowed to concentrate to the point where lead chlorid crystallizes out.

METHOD III.

Total arsenic present as As_2O_3 only.

As the amount of As_2O_3 in lead arsenate is usually very small, weigh an amount of the powdered sample equal to 10 times the amount of arsenic trioxid (As_2O_3) to which 100 cc. of the iodin solution are equivalent. Transfer to a 200 cc. graduated flask, add about 100 cc. of water and 3 to 4 cc. of concentrated sulphuric acid, boil for a few minutes, cool, make to volume, shake thoroughly, filter through a dry filter, take 100 cc. of the filtrate, add sodium bicarbonate in excess and about 5 cc. of starch solution, and titrate with standard iodin solution in the usual way. The number of cubic centimeters of iodin solution used in this titration divided by 5 equals the per cent of arsenic trioxid (As_2O_3) in the sample.

The coöperating chemists report the following results:

Analyses of lead arsenate.

ANALYST	TOTAL ARSENIC AS As_2O_5			
	Method I (a)	Method I (b)	Method II	Distillation
	per cent	*per cent*	*per cent*	*per cent*
Hugh L. Fulmer, Guelph, Canada	31.85	31.95	32.68	32.10
	32.00	31.90	32.48	32.20
	31.53	.....	32.75	.....
	31.35	.....	32.43	.....
Average	31.68	31.93	32.59	32.15
A. C. Whittier, Newark, Del	32.35	32.25	32.05	.....
	31.95	32.25	32.10	.....
	32.45	31.85	32.00	.....
Average	32.25	32.12	32.05	.....
W. L. Latshaw and J. C. Ripperton, Manhattan, Kans.	32.10	32.30	32.15	.....
	32.15	32.20	32.00	.....
Average	32.13	32.25	32.08	.....
A. J. Flume, Geneva, N. Y	32.10	32.52	32.50	.....
	31.92	32.60	32.90	.....
	32.25	32.62	33 00	.....
	32.05	32.70	32.55	.....
	.....	32.75	32.45	.....
	.....	.....	32.65	.....
Average	32.08	32.64	32.68	.....
A. L. Sherman, Pullman, Wash	32.01	32.00	31.85	.....
	32.07	.....	31.93	.....
Average	32.04	32.00	31.89	.....
F. L. Elliott, Washington, D. C	31.90	31.93	32.03	.....
	31.90	31.80	32.03	.....
	31.85	31.80	.....	.....
Average	31.88	31.84	32.03	.....
J. J. T. Graham, Washington, D. C	31.95	32.00	31.88	.....
	31.80	31.90	31.90	.....
	31.83	32.05	31.98	.....
Average	31.86	31.98	31.92	.....
W. J. Morgan, Washington, D. C	31.55	31.73	32.03	.....
	31.45	31.63	32.10	.....
	31.50	31.88	.....	.....
Average	31.50	31.75	32.07	.....
E. J. Nealon, Washington, D. C	31.75	31.70	32.09	.....
	31.73	31.65	32.04	.....
	.....	31.65	32.07	.....
	.....	31.55	32.07	.....
Average	31.74	31.64	32.07	.....

Analyses of lead arsenate—Continued.

ANALYST	TOTAL ARSENIC AS As_2O_5			
	Method I (a)	Method I (b)	Method II	Distillation
	per cent	*per cent*	*per cent*	*per cent*
C. H. Walker, Washington, D. C.	32.11	32.08	32.12	.....
	32.11	32.08	32.16	.....
Average	32.11	32.08	32.14	.....
R. C. Roark, Washington, D. C.	31.90	32.00	32.10	32.00
	31.80	31.95	32.03	32.00
	31.85	31.85	32.10	.....
Average	31.85	31.93	32.08	32.00
Dean C. Kellog, East Lansing, Mich.	32.65	32.60	.....	32.70
	32.60	32.80	.....	32.70
Average	32.63	32.70	.....	32.70
George E. Holm, St. Paul, Minn.	32.50	32.90	32.20	.....
	32.45	33.12	32.26	.....
Average	32.48	33.01	32.23	.....
W. H. Rogers and E. R. Tobey, Orono, Me.	31.60	.....	31.97	.....
	31.66	.....	32.05	.....
	31.70	.....	.....	.....
	31.75	.....	.....	.....
Average	31.68	.....	32.01	.....
E. E. Sawyer, Orono, Me.	31.45	.....	32.42	.....
	31.45	.....	32.62	.....
Average	31.45	.....	32.52	.....
General average	31.92	32.13	32.22	32.28

Methods I (a) and I (b) for total arsenic in lead arsenate are slight modifications of the present official method (U. S. Bur. Chem. Bul. 107 (rev.), p. 237). Method II is here presented to the association for the first time. It is based on the following reaction, which was first studied by Naylor (Pharm. J. and Trans., 1879, (3), **10**: 441–442):

$$As_2O_5 + 4HI = As_2O_3 + 4I.$$

COMMENTS BY ANALYSTS.

W. L. Latshaw and *J. C. Ripperton:* In Methods I (a) and I (b) it was found that heating with sulphuric acid in a casserole for two hours, instead of heating until white fumes were evolved, increased the results 0.5% or more.

A. L. Sherman (speaking of Method II for the determination of arsenic as As_2O_5 only): I found it was very important to obey all minute precautions throughout this determination. Temperature is an extremely important factor.

In the following table are presented results by the present official, the distillation, and the thiosulphate (II) methods on a number of commercial lead arsenates, as well as on some lead arsenates prepared in the Insecticide and Fungicide Laboratory.

Results on various lead arsenates.

LABORATORY NO.	DESCRIPTION	TOTAL ARSENIC AS As_2O_5		
		Official method	Distillation method	Method II
		per cent	*per cent*	*per cent*
11548	Commercial sample	29.19	.....	29.10
		29.15	.....	29.15
	Average	29.17	.....	29.13
11549	Commercial sample	25.76	25.65	25.25
		25.69	25.60	25.25
	Average	25.73	25.63	25.25
11550	Commercial sample	28.42	28.70	28.80
		28.21	28.60	28.70
	Average	28.32	28.65	28.75
11552	Commercial sample	30.44	30.50	31.10
		30.73	30.50	31.15
		.....	.....	31.23
	Average	30.59	30.50	31.16
14604	Commercial sample	27.48	.....	27.70
		27.59	.....	27.75
	Average	27.54	.....	27.73
17730	Commercial sample	30.00	.....	30.40
		30.00	.....	30.38
	Average	30.00	.....	30.39
20076	Commercial sample	31.31	.....	31.50
		31.45	.....	31.50
	Average	31.38	.....	31.50
20232	Commercial sample	28.71	.....	28.93
		28.67	.....	28.98
	Average	28.69	.....	28.96
20346	Commercial sample	28.26	.....	28.33
		28.18	.....	28.35
	Average	28.22	.....	28.34
20350	Commercial sample	30.93	.....	30.95
		31.05	.....	30.95
	Average	30.99	.....	30.95

Results of various lead arsenate—Continued.

LABORATORY NO.	DESCRIPTION	METHOD		
		Official method	Distillation method	Method II
		per cent	*per cent*	*per cent*
20479	Commercial sample	32.37	.....	32.60
		32.28	.....	32.55
	Average	32.33	.....	32.58
20832-A	Commercial sample	.....	29.30	29.65
		.....	29.10	29.55
	Average	.....	29.20	29.60
20832-B	Commercial sample	.....	29.80	29.55
		.....	29.90	29.45
	Average	.....	29.85	29.50
20832-C	Commercial sample	.....	29.75	29.65
		.....	29.70	29.70
	Average	.....	29.73	29.68
20832-D	Commercial sample	.....	29.50	29.75
		.....	29.40	29.80
	Average	.....	29.45	29.78
21165	Commercial sample	31.63	31.70	32.30
		31.46	31.60	32.30
		.....	.....	32.25
	Average	31.55	31.65	32.28
C	Lead arsenate[1]	22.96	.....	22.90
		22.89	.....	22.88
	Average	22.93	.....	22.89
D	Lead arsenate[1]	32.29	.....	32.45
		31.86	.....	32.45
	Average	32.08	.....	32.45
E	Lead arsenate[1]	22.96	23.50	23.45
		22.89	23.50	23.48
	Average	22.93	23.50	23.47
F	Lead arsenate[1]	22.96	.....	23.10
		22.82	.....	23.15
		.....	.....	23.25
	Average	22.89	.....	23.17
G	Lead arsenate[1]	30.17	.....	30.55
		30.52	.....	30.55
	Average	30.35	.....	30.55

[1] Prepared in the Insecticide and Fungicide Laboratory.

Results of varions lead arsenate—Continued.

LABORATORY NO.	DESCRIPTION	METHOD		
		Official method	Distillation method	Method II
		per cent	*per cent*	*per cent*
	Dilead arsenate ($PbHAsO_4$)[1]	.....	33.14	33.10
		.....	33.10	33.15
	Average	.....	33.12	33.13
	Dilead arsenate ($PbHAsO_4$)[2]	33.08	33.08	33.18
		33.13	33.05	33.18
		.....	.....	33.15
	Average	33.11	33.07	33.17
	Basic lead arsenate[2]	23.63	23.59	23.70
		23.65	23.56	23.69
	Average	23.59	23.58	23.70
	Lead chlor arsenate[2]	23.63	23.63	23.64
		23.63	23.60	23.62
		.....	.....	23.61
	Average	23.63	23.62	23.62
	1909 A. O. A. C. lead arsenate	30.93	30.86	30.90
		30.78	30.85	30.93
		30.93	.....	.....
		30.78	.....	.....
	Average	[3]30.86	30.85	30.92
	1910 A. O. A. C. lead arsenate	31.98	31.80	32.00
		31.62	31.80	31.98
		31.78	.....	.....
	Average	[4]31.79	31.80	31.99

[1] Prepared by C. M. Smith (theory = 33.11% As_2O_5).
[2] Prepared by J. J. T. Graham.
[3] Results by W. B. Pope (U. S. Bur. Chem. Bul. 132, p. 45.)
[4] Results by R. C. Roark, (U. S. Bur. Chem. Bul. 137, p. 37.

LEAD ARSENATE WITH LEAD ARSENITE.

This sample was prepared by mixing known quantities of lead arsenate and lead arsenite. It was designed to test Method III for total arsenic in lead arsenate present as As_2O_3 only, but through a misunderstanding some of the coöperators made this determination on the sample of lead arsenate alone—a sample which contains only a trace, if any, arsenic as As_2O_3.

The results obtained are as follows:

Results on lead arsenate with lead arsenite.

ANALYST	TOTAL ARSENIC AS As_2O_5			As_2O_5 ONLY	As_2O_3 ONLY
	Method I (a)	Method I (b)	Distillation method		
Dean C. Kellog, East Lansing, Mich.	30.60	30.60	.....	21.35	5.76
	30.50	30.60	.....	21.60	5.78
	.....	30.50	.....	21.57	5.76
Average	30.55	30.57	.....	21.51	5.77
R. C. Roark, Washington, D. C.	.....	.....	30.48	21.65	7.60
	.....	.....	30.50	21.55	7.44
	.....	.....	.....	21.60	.....
Average	.....	.....	30.49	21.60	7.52
Hugh L. Fulmer, Guelph, Canada	.....	.....	.....	.....	5.88
	.....	.....	.....	.....	5.83
Average	.....	.....	.....	.....	5.86
A. J. Flume, Geneva, N. Y.	.....	.....	.....	.....	6.35
	.....	.....	.....	.....	6.34
	.....	.....	.....	.....	6.25
	.....	.....	.....	.....	6.34
Average	.....	.....	.....	.....	6.32
Geo. E. Holm, St. Paul, Minn.	30.75	30.70	.....	21.80	7.54
	31.10	30.50	.....	21.76	7.54
Average	30.93	30.60	.....	21.78	7.54
W. H. Rogers and E. R. Tobey, Orono, Me.	.....	.....	.....	21.35	6.11
	.....	.....	.....	21.27	6.20
Average	.....	.....	.....	21.31	6.16
General average	30.74	30.58	30.49	21.55	6.45
Calculated	30.48	30.48	30.48	21.48	7.75

DISCUSSION OF RESULTS.

The results for As_2O_3 are rather discrepant, which may be accounted for in the varying lengths of time the sample was boiled with sulphuric acid. A. J. Flume says in regard to this: "If the samples are boiled less than five minutes with the H_2SO_4, the results are not reliable."

This sample was prepared by mixing 400 grams of the lead arsenate used for the association work this year with 200 grams of lead arsenite. According to the analysis of the referee, this lead arsenite contained:

	Per cent As_2O_3
Total arsenic as As_2O_3	23.63
(Distillation method)	23.66
Average	23.65
As_2O_5 only 0.45	
(Method II for lead arsenate) 0.45	= 0.39
Total As_2O_3 present, by difference	23.26
As_2O_3 found directly by Method III	23.15

If we take the composition of the 1915 association sample of lead arsenate as 32.00% As_2O_5 with no As_2O_3 present, the sample of lead arsenate with lead arsenite would have the following composition:

$$\text{Total arsenic (calculated as } As_2O_5) = 30.48$$

$$As_2O_5 \text{ only } \frac{(2 \times 32.00) + (1 \times 0.45)}{3} = 21.48$$

$$As_2O_3 \text{ only } \frac{23.26}{3} = 7.75$$

$$7.75\ As_2O_3 = 9.00\ As_2O_5$$
$$21.48\ As_2O_5 = 18.69\ As_2O_3$$

The referee recommends that the method for the determination of As_2O_3 only be further studied, increasing the time of heating to 20 to 30 minutes and the amount of concentrated sulphuric acid to not less than 5 cc. to 1 gram of sample.

The referee also wishes to recommend the distillation method as an official one for the determination of total arsenic in a lead arsenate. It has been found to yield the best results and with the least trouble.

An amount of the sample equal to 5 times the amount of arsenic pentoxid to which 100 cc. of the standard iodin solution are equivalent should be used, and a titration made on one-fifth of the distillate. In this way the number of cubic centimeters of iodin solution used in the titration represents directly the total per cent of arsenic in the sample expressed as arsenic pentoxid (As_2O_5).

In regard to Methods I (a) and I (b), as well as the present official method (U. S. Bur. Chem. Bul. 107 (rev.), p. 239), while they yield good results on a comparatively pure lead arsenate, they would determine antimony if present, and in the presence of chlorids arsenic present as As_2O_3 might be lost through volatilization of $AsCl_3$. Most lead arsenates will contain a small amount of arsenite, and there is reason to believe that antimony may be occasionally present. Moreover, in analyzing lead chlor-arsenates, such as those prepared by McDonnell and Smith, where chlorin is a part of the molecule, the danger of loss of arsenic as $AsCl_3$, is still greater. The referee, therefore, recommends that these methods be discarded and the distillation method be substituted therefor.

In regard to Method II, while this yields most excellent results on pure samples and even in the presence of As_2O_3, it is inapplicable in the pres-

ence of copper and is affected by any substance that will liberate iodin from an acid solution, e.g., ferric chlorid, nitrates, etc. It will also determine any antimony present as Sb_2O_5. As the method is so very quick and simple, the referee recommends that it be further studied, special attention being given to the effect of various impurities that may be present in commercial lead arsenates.

A temperature of 35° to 40°, as called for in this method, is not essential, as we have found a temperature of 20° to 25° gives equally as good results. The standardization and determination should, however, be carried out at the same temperature.

The referee has found that more accurate results are obtained when the thiosulphate solution is standardized directly against a pure lead arsenate or other arsenate, rather than against a standard iodin solution. A pure diplumbic hydrogen arsenate may be prepared as follows:

Precipitate diplumbic arsenate by the addition of a solution of lead nitrate to a solution of potassium dihydrogen arsenate (KH_2AsO_4) which should be in excess. Collect the precipitate by filtration and dissolve in boiling 1 to 4 nitric acid, adding enough of the lead arsenate to secure a completely saturated solution while boiling hot, then filter rapidly through a folded paper filter, and pour the filtrate into 10 to 12 times its volume of cold distilled water. The precipitate should be collected by filtration, dried, powdered, thoroughly dried at 110°, and kept in a glass-stoppered weighing bottle.

Prepared in this way the lead arsenate should have the formula $PbHAsO_4$, in which the theoretical content of arsenic pentoxid (As_2O_5) is 33.11%. A lead arsenate of known composition is particularly valuable in checking the strength of the thiosulphate solution, but may be used also in the distillation method to check the value of the iodin solution.

CALCIUM ARSENATE.

TOTAL ARSENIC.

METHOD I.

Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 11, paragraph 32.

METHOD II.

Total arsenic present as As_2O_5 only.

Determine as directed in Method II for lead arsenate, using, however, an amount of the powdered sample just equal to the amount of arsenic pentoxid (As_2O_5) to which 100 cc. of the thiosulphate solution are equivalent.

The results obtained by the chemists coöperating in this work are as follows:

Results on calcium arsenate.

ANALYST	TOTAL ARSENIC AS As_2O_5	
	Method I	Method II
	per cent	*per cent*
Hugh L. Fulmer, Guelph, Canada	55.50	56.40
	55.70	56.40
Average	55.60	56.40
C. H. Robinson, Ottawa, Canada	57.25	57.80
	57.30	57.75
	57.20	57.70
Average	57.25	57.75
A. C. Whittier, Newark, Del	56.60	55.60
	56.60	55.70
	56.80	55.90
Average	56.67	55.73
W. L. Latshaw and J. C. Ripperton, Manhattan, Kans.	55.60	55.80
	55.60	55.50
	.....	55.50
	.....	55.80
Average	55.60	55.65
A. J. Flume, Geneva, N. Y.	56.51	56.50
	56.19	56.40
	56.59	56.50
	.....	56.40
Average	56.43	56.45
R. C. Roark, Washington, D. C.	55.90	55.90
	55.85	55.90
	.....	55.90
Average	55.88	55.90
Dean C. Kellog, East Lansing, Mich.	56.00	55.60
	56.20	55.60
Average	56.10	55.60
W. H. Rogers and E. R. Tobey, Orono, Me.	55.32	55.30
	55.50	.....
Average	55.41	55.30
General average	56.22	56.18

The recommendations made in regard to the methods for lead arsenate apply equally to the methods for calcium arsenate.

ZINC ARSENITE.

TOTAL ZINC OXID (ZnO).

METHOD I.

To 0.5 gram of the powdered sample add 20 cc. of a mixture of equal amounts of hydrobromic acid (specific gravity 1.31) and hydrochloric acid (specific gravity 1.19) and evaporate to dryness. Repeat until all arsenic is removed (two evaporations are usually sufficient), then evaporate to dryness with concentrated hydrochloric acid. Dissolve in 25 cc. of 2N HCl, dilute to 100 cc., and pass in hydrogen sulphid until all lead, antimony, and remaining traces of arsenic are precipitated. Filter, wash precipitate thoroughly with N/2 HCl saturated with hydrogen sulphid, and concentrate the filtrate to small volume by boiling. When the solution is free from hydrogen sulphid, add 1 or 2 cc. of concentrated nitric acid and boil a few minutes to oxidize all Fe^{II} to Fe^{III}, then precipitate the iron with ammonium hydroxid. Filter, wash precipitate thoroughly with hot water, then redissolve the precipitate in a little hot dilute nitric acid, collecting in a dry beaker, and reprecipitate the iron as before, filter, wash precipitate thoroughly with hot water, combine both filtrates and washings, add an excess of concentrated nitric acid, and evaporate to dryness on the steam bath to remove ammonium salts. Take up in water, together with a little hydrochloric acid, cool, add 10% sodium carbonate solution drop by drop until the zinc solution becomes turbid; then transfer to a porcelain casserole and heat to boiling for a few minutes. Now add a few drops of phenolphthalein solution and sufficient sodium-carbonate solution to produce a distinct pink color, boil for a minute or two longer, then filter from the hot solution. The precipitate should be washed with hot water, first by decantation and then on the filter. The thoroughly washed precipitate on the filter is dried, then carefully ignited (preferably in a muffle), and finally heated over a Bunsen burner. From the weight of the ignited zinc oxid calculate the per cent of zinc oxid (ZnO) in the sample.

(NOTE.—This method is not applicable in the presence of calcium.)

METHOD II.

(Method of Balls and McDonnell.[1])

Dissolve 0.5 gram of the powdered sample in dilute sulphuric acid (1:5), add 50% KOH solution to 20 grams excess KOH, oxidize all the arsenic to As^{V} with a little sodium peroxid, transfer to a weighed nickel crucible of about 125 cc. capacity, and electrolyze, using a rotating anode. The anode rotation should be about 600 revolutions perminute, and the current 3 to 4 amperes per 100 sq. cm. of cathode surface. When the zinc is all deposited, which should take 1 to 2 hours, wash the deposit before interrupting the current by siphoning, then rinse with alcohol and dry to constant weight at 110° in an oven. From the weight of metallic zinc calculate the per cent of zinc oxid (ZnO) in the sample. Factor: $Zn \times 1.24476 = ZnO$.

(NOTE.—If the deposit shows a tendency to be spongy, this may be overcome by adding 2 or 3 cc. of a mixture of equal parts of glycerol and ethyl alcohol.)

---

[1] J. Ind. Eng. Chem., 1915, **7**: 26–29.

TOTAL ARSENIC.

METHOD I.

Total arsenic present as As_2O_3 and As_2O_5.

Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 11, paragraph 33.

METHOD II.

Total arsenic present as As_2O_3 and As_2O_5.

Weigh carefully an amount of the powdered sample equal to five times the amount of arsenic trioxid (As_2O_3) to which 100 cc. of the standard iodin solution are equivalent, transfer to a 250 cc. graduated flask, dissolve in about 100 cc. dilute acetic acid (10 parts glacial acetic acid to 90 parts water), heating to boiling if necessary, then add 4 to 5 grams oxalic acid. Continue the heating for a few minutes, then cool, make to volume, shake thoroughly, filter through a dry filter, pipette 100 cc. of the clear filtrate into an Erlenmeyer flask, add 3 to 4 cc. concentrated sulphuric acid and 1 gram KI, boil down to about 40 cc., cool, remove excess iodin with a few drops of N/20 thiosulphate, then add sodium bicarbonate in excess, and titrate with standard iodin solution in the usual way. The number of cubic centimeters of iodin used in this titration divided by 2 represents directly the total per cent of arsenic in the sample expressed as As_2O_3.

(NOTE.—In case antimony is present it will be determined and reported as As_2O_3 according to this method.)

METHOD III.

Total arsenic present as As_2O_3 only.

(a) Proceed exactly as directed under (a) Method III for total arsenic in Paris green.

(b) Proceed exactly as directed under (b) Method III for total arsenic in Paris green.

(In either case, as the content of As_2O_3 in zinc arsenite is less than 50%, the iodin must be added from a burette and not from a 50 cc. pipette.)

METHOD IV.

Total arsenic present as As_2O_5 only.

Determine as directed under Method II for total arsenic in lead arsenate. As the amount of As_2O_5 in zinc arsenite is usually small, weigh an amount of the powdered sample equal to 5 to 10 times the amount of arsenic oxid (As_2O_5) to which 100 cc. of the standard thiosulphate solution are equivalent. If iron salts are present the hydrochloric-acid solution will be colored, and the use of starch paste is necessary to determine the end point in the thiosulphate titration. The standardization of the thiosulphate solution should be made with the aid of starch paste also, if it is used in the determination.

(NOTE—If any antimony is present as Sb_2O_5 it will be determined and reported as As_2O_5 according to this method.)

The results obtained on this sample are as follows:

Results on zinc arsenite.

ANALYST	ZINC OXID		TOTAL ARSENIC AS As_2O_3				As_2O_5
	Method I	Method II	Method I	Method II	Method III (a)	Method III (b)	Method IV
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
C. H. Robinson, Ottawa, Canada...	54.64	.....	42.30	42.50	41.50	42.00	0.50
	54.88	.....	42.00	42.42	41.55	42.05	0.48
	.....	.....	42.18	42.47	41.45	42.10	0.47
	.....	.....	42.12	42.40	.....	.....	.....
Average.....	54.76	.....	42.15	42.45	41.50	42.05	0.48
Hugh L. Fulmer, Guelph, Canada..	.....	.....	42.20	42.80	41.80	42.05	0.77
	.....	.....	41.70	42.85	41.90	42.05	0.73
	.....	.....	.....	.....	41.70	.....	.....
Average.....	.....	.....	41.95	42.83	41.80	42.05	0.75
A. C. Whittier, Newark, Del.....	.....	.....	42.10	43.50	42.80	43.00	0.78
	.....	.....	42.20	43.50	42.80	42.60	0.77
	.....	.....	.....	.....	43.20	43.20	0.81
Average.....	.....	.....	42.15	43.50	42.93	42.93	0.79
W. L. Latshaw and J. C. Ripperton, Manhattan, Kans.	.....	.....	41.80	42.37	42.30	42.20	0.79
	.....	.....	41.80	42.27	42.20	42.10	0.79
	.....	.....	.....	42.30	.....	.....	0.79
Average.....	.....	.....	41.80	42.31	42.25	42.15	0.79
Dean C. Kellog, East Lansing, Mich.	54.96	55.30	42.40	42.50	41.60	.....	0.94
	54.74	56.38	42.40	42.52	41.50	.....	0.94
	54.36	55.16	.....	42.50	.....	.....	.....
	.....	54.72	.....	.....	.....	.....	.....
Average.....	54.69	55.39	42.40	42.51	41.55	.....	0.94
A. J. Flume, Geneva, N. Y.....	.....	.....	42.65	43.00	42.50	41.70	0.74
	.....	.....	42.88	43.30	42.25	42.10	0.71
	.....	.....	42.66	43.15	42.00	41.90	.....
	.....	.....	.....	43.00	42.00	42.20	.....
Average.....	.....	.....	42.73	43.11	42.19	41.98	0.73
F. L. Elliott, Washington, D. C.....	56.36	56.72	41.72	42.64	41.80	41.80	0.80
	56.52	56.72	41.65	42.64	41.90	41.80	0.76
	57.06	.....	.....	42.51	41.80	41.90	0.77
	57.00	.....	.....	.....	.....	.....	.....
Average.....	56.74	56.72	41.69	42.60	41.83	41.83	0.78
J. J. T. Graham, Washington, D. C.	.....	.....	41.59	42.48	41.80	41.85	0.70
	.....	.....	41.98	42.48	41.85	41.85	0.77
	.....	.....	41.59	42.58	41.85	41.75	0.73
	.....	.....	41.63	.....	.....	.....	.....
Average.....	.....	.....	41.70	42.51	41.83	41.82	0.73
W. J. Morgan, Washington, D. C...	.....	.....	41.85	.....	.....	.....	.....
	.....	.....	42.05	.....	.....	.....	.....
Average	.....	.....	41.95	.....	.....	.....	.....

Results on zinc arsenite—Continued.

ANALYST	ZINC OXID		TOTAL ARSENIC AS As_2O_3				As_2O_5
	Method I	Method II	Method I	Method II	Method III (a)	Method III (b)	Method IV
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
E. J. Nealon, Washington, D. C...	55.48	.....	41.98	42.18	.....	41.70	.....
	55.26	.....	41.85	42.31	.....	41.70	.....
Average.....	55.37	.....	41.92	42.25	.....	41.70	.....
C. H. Walker, Washington, D. C....	56.35	56.34	41.37	42.48	41.23	41.42	0.72
	56.10	56.49	41.34	42.55	41.23	41.52	0.68
Average.....	56.23	56.42	41.36	42.52	41.23	41.47	0.70
R. C. Roark, Washington, D. C.....	55.34	.....	41.80	42.44	41.80	41.80	0.74
	55.00	.....	41.69	42.18	41.80	41.80	0.78
	.....	.....	.....	42.31	41.70	41.70	0.78
Average.....	55.17	.....	41.75	42.31	41.77	41.77	0.77
W. H. Rogers and E. R. Tobey, Orono, Me.	.....	.....	42.32	42.59	41.40	41.63	0.70
	.....	.....	42.45	42.45	41.45	.....	0.72
Average.....	.....	.....	42.39	42.52	41.43	41.63	0.71
General average.....	55.60	55.98	42.01	42.61	41.89	41.98	0.74

DISCUSSION.

Mr. O. B. Winter of the Michigan Agricultural Experiment Station, comments as follows:

The methods, with the exception of the two for the determination of zinc oxid, seemed quite satisfactory. In Method II, the anode used was about 5 cm. in diameter, perforated, and made about 150 revolutions per minute. We used a low current at first, and then increased to $2\frac{1}{2}$ to 3 amperes. This was not according to directions and may account for the inconsistent results. In Method I, the solution showed that not all the impurities were removed. This may explain the high results.

C. H. Walker, of the Bureau of Chemistry, Washington, D. C., also determined the zinc oxid by titration with potassium ferrocyanid according to the method of C. Fahlberg (Fresenius Quantitative Analysis 1911, **2**: 443–444) and by electrolysis in potassium-hydroxid solution in a nickel crucible after the removal of arsenic, lead, and antimony according to Method I, page 174. By titration he obtained 56.76%, 56.70%, and 56.83%, and by electrolysis, 56.23% and 56.30% ZnO. The referee is of the opinion that electrolysis of the zinc after the removal of arsenic, lead, and antimony will be found to be a much better procedure than that of Balls and McDonnell.

This sample contains a small amount of antimony as Sb_2O_5. The figures in the column headed "As_2O_5, Method IV" multiplied by the factor 1.39353 will give the percentages of Sb_2O_5, the average being 1.03% The differences in the results for arsenic trioxid (As_2O_3) by Methods I and II are due to the antimony, which is determined by Method II, but not by the distillation method, or Method I of the table. The average difference in the results by these two methods is 0.60% As_2O_3, which calculated to As_2O_5 gives 0.70%, a figure that agrees very closely with 0.74%, the average of the results by Method IV for As_2O_5 only (really Sb_2O_5).

Results for arsenic trioxid (As_2O_3) only by the modified methods of C. C. Hedges and C. M. Smith (Methods III (a) and III (b) of the table) agree almost exactly with those for total arsenic by the distillation method. This shows that all the arsenic is present as As_2O_3 and all the antimony as Sb_2O_5; furthermore, that the distillation method effectively separates a large amount of arsenic from a small amount of antimony.

The only one of the methods for the analysis of zinc arsenite which the referee wishes to recommend for official adoption is the distillation method for total arsenic. It is recommended that Method II for total arsenic be discarded and that the methods for zinc oxid be further studied. The other methods have been spoken of under Paris green and lead arsenate.

BORDEAUX MIXTURE.

(1) *Moisture.*—Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 11, paragraph 36.

(2) *Carbon dioxid.*—Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 12, paragraphs 37–38.

(3) *Copper.*—Electrolytic method: Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 12, paragraph 39.

Thiosulphate method: Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 12, paragraph 40.

The results on this sample follow:

Results on Bordeaux mixture.

ANALYST	MOISTURE	CARBON DIOXID	COPPER	
			Electrolytic	Thiosulphate
	per cent	*per cent*	*per cent*	*per cent*
A. C. Whittier, Newark, Del.	4.20	12.72	.....	12.98
	4.24	12.70	.....	12.91
	.....	.....	.....	12.96
Average	4.22	12.71	.....	12.95

Results on Bordeaux mixture—Continued.

ANALYST	MOISTURE	CARBON DIOXID	COPPER	
			Electrolytic	Thiosulphate
	per cent	*per cent*	*per cent*	*per cent*
R. C. Roark, Washington, D. C.	4.57	12.68	12.77	12.90
	4.72	12.73	12.85	12.83
Average	4.65	12.71	12.81	12.87
A. J. Flume, Geneva, N. Y.	.....	.....	.....	12.87
	.....	.....	.....	12.90
	.....	.....	.....	12.87
	.....	.....	.....	12.87
Average	.....	.....	.....	12.88
W. H. Rogers and E. R. Tobey, Orono, M.	4.84	12.55	13.03	13.07
	.....	12.69	13.04	13.13
Average	4.84	12.62	13.04	13.10
General average	4.51	12.68	12.92	12.94

BORDEAUX MIXTURE WITH PARIS GREEN.

(1) *Moisture.*—Determine as directed for Bordeaux mixture.

(2) *Carbon dioxid.*—Determine as directed for Bordeaux mixture.

(3) *Copper.*—Electrolytic method: Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 13, paragraph 44.

Thiosulphate method: Weigh 2 grams of the dry powdered sample, transfer to an Erlenmeyer flask, add 25 cc. of concentrated nitric acid, and heat on the steam bath to disappearance of brown fumes. Dilute somewhat with water and boil for several minutes, then add 10 cc. of bromin water and continue boiling until all bromin is expelled. Neutralize with concentrated ammonium hydroxid and add about 5 cc. in excess. Boil a minute or so and add acetic acid in excess. Cool thoroughly, add about 3 grams of KI (or 10 cc. of KI solution, 30 grams to 100 cc.), and titrate immediately with standard thiosulphate solution in the usual way. Be careful that copper remains in solution. If copper appears to precipitate, it may be redissolved by the addition of a little acetic acid and rubbing the precipitate with a stirring rod fitted with a rubber policeman. Near the end of the titration it is well to add the starch solution in successive small quantities.

(4) *Arsenic trioxid* (As_2O_3).—Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 13, paragraph 45.

C. C. Hedges method, modified: Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 13, paragraph 46.

C. M. Smith method, modified: Proceed as directed above, using dilute sulphuric acid (1 to 4) instead of dilute hydrochloric. The solution in this case may be heated to boiling.

(5) *Water-soluble arsenious oxid* (As_2O_3).—Treat 2 grams with 1,000 cc. distilled water, digesting for 24 hours at a temperature of 32°C., shaking 8 times during the

day at intervals of 1 hour. Filter through a dry filter, take a 250 cc. aliquot, make slightly acid with HCl (methyl orange as indicator), then alkaline with excess of sodium bicarbonate, and titrate with N/20 iodin as usual. Make corrections for iodin necessary to produce the same color, using same chemicals and same volume.

Calculate all results to original material.

The results of the coöperators on this sample are as follows:

Results on Bordeaux mixture with Paris green.

ANALYST	MOISTURE	CARBON DIOXID	COPPER		TOTAL ARSENIC AS As_2O_3			WATER-SOLUBLE As_2O_3
			Electrolytic	Thiosulphate	Distillation method	Hedges method	Smith method	
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A. C. Whittier, Newark, Del.	3.56	2.59	.....	16.77	31.60	.....	30.10	[1]1.22
	4.03	2.66	.....	18.15	31.45	.....	30.15	[1]1.22
	3.48	2.62	.....	17.91	31.45	.....	30.60	[1]1.22
Average	3.69	2.62	.....	17.61	31.50	.....	30.28	1.22
W. L. Latshaw and J. C. Ripperton, Manhattan, Kans.	.....	.....	.....	.....	31.30	31.40	.....	.....
	.....	.....	.....	.....	31.20	31.30	.....	.....
Average	.....	.....	.....	.....	31.25	31.35	.....	.....
A. J. Flume, Geneva, N. Y.	.....	.....	.....	17.22	31.95	.....	.....	.....
	.....	.....	.....	17.29	32.25	.....	.....	.....
	.....	.....	.....	17.19	32.50	.....	.....	.....
	.....	.....	.....	.....	32.55	.....	.....	.....
Average	.....	.....	.....	17.23	32.31	.....	.....	.....
R. C. Roark, Washington, D. C.	3.35	2.55	18.80	18.53	31.93	31.80	31.80	1.89
	3.33	2.65	.....	18.50	.....	31.85	32.00	1.92
	.....	.....	.....	.....	.....	31.90	31.80	1.88
Average	3.34	2.60	18.80	18.52	31.93	31.85	31.87	1.90
George E. Holm, St. Paul, Minn.	.....	.....	.....	.....	32.00	.....	31.78	1.81
	.....	.....	.....	.....	31.96	.....	31.80	1.82
Average	.....	.....	.....	.....	31.98	.....	31.79	1.82
W. H. Rogers and E. R. Tobey, Orono, Me.	2.94	[1]3.48	.....	20.15	31.53	.....	32.30	[1]2.41
	.....	[1]3.43	.....	20.33	31.23	.....	32.50	[1]2.51
	.....	[1]3.48	.....	.....	.....	.....	32.40	.....
Average	2.94	3.46	.....	20.24	31.41	.....	32.40	2.46
General average	3.45	2.61	18.80	18.20	31.78	31.65	31.57	1.86
Calculated	.....	.....	18.83	.....	31.98	.....	.....	.....

[1] Omitted from the general average.

This sample was prepared by thoroughly mixing 293.5 grams of the 1914 association sample dry Bordeaux with 348.5 grams of the 1914 association sample Paris green. By the distillation method this Paris

green was shown to contain 58.91% to 58.93%, average 58.92%, As_2O_3. The Bordeaux-Paris green should therefore contain 31.98% As_2O_3.

By separating the copper from the arsenic by precipitation with sodium hydroxid and electrolyzing it in nitric-acid solution, the 1914 association sample of Paris green yielded 23.27%, 23.37%, average 23.32%, copper (Cu). Taking the general average of all results on the 1914 association dry Bordeaux for copper by the electrolytic method, which is 13.49%, the calculated amount of copper in the 1915 association Bordeaux-Paris green is 18.83%.

Mr A. C. Whittier, of the Delaware Agricultural Experiment Station, makes the following comments:

> I used approximately an N/20 solution of sodium thiosulphate and got titrations of 108.8, 117.8, and 116.2 cc. I could get no real permanent end point, the blue color very slowly reappearing after each addition of thiosulphate, after 100 cc. had been added.
>
> The determination was repeated, using 1 gram instead of 2 grams. Great care was necessary to procure a permanent end point. The thiosulphate was added until no blue color returned after standing one minute.

The results obtained by Mr. Whittier, using different amounts of sample (thiosulphate method) are as follows:

	Per cent copper
2-gram sample	16.77
	18.15
	17.91
Average	17.61
1-gram sample	18.80
	18.86
	18.83
Average	18.83

The results on the 1-gram sample agree closely with the value determined by the electrolytic method by the referee.

The referee found that if distilled water which had been recently boiled and cooled was used instead of ordinary distilled water in determining the water-soluble arsenic in this sample, percentages of 2.15, 2.12, and 2.12 As_2O_3 were obtained. That these results should be higher was somewhat surprising, and emphasize the importance of following the method closely in every detail. Temperature is one of the most important factors in determining water-soluble arsenic and should be closely watched. In order that the water may be at 32° at the beginning of the digestion, it should be kept at this temperature for some time before adding the sample to be tested.

These methods were studied last year. The referee wishes to recommend that the methods for moisture, carbon dioxid, total arsenic by the distillation method, and water-soluble arsenic be adopted as official and that the other methods be further studied.

BORDEAUX MIXTURE WITH LEAD ARSENATE.

(1) *Moisture.*—Determine as directed for Bordeaux mixture.

(2) *Carbon dioxid.*—Determine as directed for Bordeaux mixture.

(3) *Copper.*—Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 13, paragraph 44.

In determining copper electrolytically in a Bordeaux-lead arsenate or a Bordeaux-Paris green, be sure that all the arsenic is in the "ic" (As^{V}) form.

(4) *Lead oxid.*—Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 14, paragraph 52.

(5) *Total arsenic pentoxid* (As_2O_5).—Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 14, paragraph 53.

(6) *Water-soluble arsenic oxid* (As_2O_5).—Proceed as directed in Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, page 11, paragraph 31.

The following results were obtained on the sample:

Results on Bordeaux mixture with lead arsenate.

ANALYST	MOISTURE	CARBON DIOXID	COPPER	LEAD OXID	TOTAL ARSENIC AS As_2O_5	WATER-SOLUBLE As_2O_5
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A. C. Whittier, Newark, Del..	2.36	7.28	.....	.....	14.10	0.20
	2.44	7.30	.....	.....	14.10	0.17
	.....	.....	.....	.....	14.15	0.20
Average.....	2.40	7.29	.....	.....	14.12	0.19
W. L. Latshaw and J. C. Ripperton, Manhattan, Kans.	.....	.....	.....	.....	14.40	.....
	.....	.....	.....	.....	14.30	.....
	.....	.....	.....	.....	14.40	.....
Average.....	.....	.....	.....	.....	14.37	.....
A. J. Flume, Geneva, N. Y....	.....	.....	.....	.....	14.75	[1]0.04
	.....	.....	.....	.....	15.00	[1]0.05
	.....	.....	.....	.....	14.75	.....
	.....	.....	.....	.....	14.80	.....
Average.....	.....	.....	.....	.....	14.83	0.05
R. C. Roark, Washington, D. C.	2.58	7.43	7.06	29.70	14.23	0.28
	2.52	7.30	6.95	29.63	14.16	0.28
Average.....	2.55	7.37	7.01	29.67	14.20	0.28
George E. Holm, St. Paul, Minn.	.....	.....	.....	.....	13.96	0.23
	.....	.....	.....	.....	13.94	0.24
Average.....	.....	.....	.....	.....	13.95	0.24
W. H. Rogers and E. R. Tobey, Orono, Me.	2.65	7.77	6.54	29.84	.....	0.30
	.....	7.86	.....	29.41	.....	0.34
Average.....	2.65	7.82	6.54	29.62	.....	0.32
General average.....	2.51	7.49	6.85	29.65	14.36	0.25
Calculated.....	.....	.....	7.02	28.99	14.32	.....

[1] Omitted from the general average.

This sample of Bordeaux-lead arsenate was prepared by thoroughly mixing 500 grams of the 1915 association Bordeaux with 405 grams of the 1915 lead arsenate. If 32% is the correct amount of arsenic oxid in this lead arsenate, then the Bordeaux-lead arsenate should contain 14.32% As_2O_5.

According to the analyses of the referee, the amount of copper in the 1915. Bordeaux is 12.71% by the electrolytic method, and the amount of lead monoxid (PbO) in the 1915 lead arsenate is 64.79% by the official chromate method. The 1915 Bordeaux-lead arsenate should contain, then, 7.02% Cu and 28.99% PbO.

The referee also determined the water-soluble As_2O_5 in this sample, using distilled water which had not been boiled to expel carbon dioxid. Great care was taken as to temperature, which was maintained at 32° C. throughout the digestion. The results were 0.94%, 0.96%, and 0.94% As_2O_5, or nearly four times as much as when carbon-dioxid-free distilled water was used.

In this connection, the referee wishes to recommend the procedure used by J. J. T. Graham, of the Insecticide and Fungicide Laboratory, in determining water-soluble arsenic in lead arsenate. After making the digestion as directed on page 182 instead of evaporating an aliquot of the filtrate with sulphuric acid to the appearance of white fumes, as directed in U. S. Bureau of Chemistry Bulletin 107 (rev.), page 240, he concentrates only to about 100 cc., then adds KI and proceeds in the usual way. This procedure saves considerable time, and the presence of leadsulphate was found not to interfere with either the reduction or titration of the arsenic.

NICOTIN.

The work on nicotin this year was a continuation of the work of 1914, namely, the comparison of the Kissling (U. S. Bur. Chem. Bul. 107 (rev.), pp. 32–33) and silicotungstic acid (U. S. Bur. Animal Indus. Bul. 133) methods. The directions for these methods are given in the Journal of the Association of Official Agricultural Chemists, volume 2 (1916), No. 1, Part II, pages 15–17, paragraphs 60–63.

One solution was sent out, on which the following results have been received:

Results on nicotin solution.

ANALYST	METHOD	
	Kissling	Silicotungstic acid
	per cent	*per cent*
C. H. Robinson, Ottawa, Canada		21.20
		21.18
		21.20
		21.21
Average		21.20
Hugh L. Fulmer, Guelph, Canada	20.51	20.94
	20.60	20.96
Average	20.56	20.95
E. L. Griffin, Washington, D. C		20.86
		20.89
Average		20.88
W. J. Morgan, Washington, D. C		20.72
E. J. Nealon, Washington, D. C		20.89
		20.91
Average		20.90
R. C. Roark, Washington, D. C	20.73	20.76
	20.72	20.81
Average	20.73	20.79
M. P. Sweeney, Geneva, N. Y		[1]20.79
		[1]20.76
		[1]20.76
		[1]20.78
		[2]20.54
		[2]20.49
		[3]20.59
		[3]20.59
Average		20.66
T. Valentine, Buffalo, N. Y		20.98
		21.09
Average		21.04
H. J. Meyers, Buffalo, N. Y		[4]20.40
		[4]20.53
		20.71
		20.81
Average		20.61
General average	20.64	20.83

[1] 2 grams distilled; 0.2 gram analyzed.
[2] 10 grams distilled; 0.5 gram analyzed.
[3] 10 grams distilled; 0.25 gram analyzed.
[4] Due to the fact that the precipitate is so profuse, it is believed that there might have been a slight loss in filtering and a low result obtained.

RECOMMENDATIONS.

It is recommended:

(1) That Method I for total arsenious oxid in Paris green (U. S. Bur. Chem. Bul. 107 (rev.), pp. 25–26), and as modified on page 157, be discarded.

(2) That the distillation method for total arsenic as described on page 158 be adopted as official and designated Method I.

(3) That the modified methods of C. C. Hedges and C. M. Smith for the determination of total arsenic as As_2O_3 only in Paris green (Methods III (a) and III (b), p. 158) be not adopted as official, but that they be used as nonofficial methods for the quick determination of the approximate amount of As_2O_3 present.

(4) That the present official method for the determination of total arsenic in lead arsenate (U. S. Bur. Chem. Bul. 107 (rev.), p. 239) and as modified (Methods I (a) and I (b), p. 163) be discarded.

(5) That the distillation method as described on page 171 be made official for the determination of total arsenic in lead arsenate.

(6) That Method II for the determination of total arsenic as As_2O_5 only in lead arsenate, pages 163–164, be further studied.

(7) That Method III, page 164, for the determination of As_2O_3 only in lead arsenate be changed so as to require a boiling of from 20 to 30 minutes with 5 cc. of concentrated sulphuric acid to each gram of sample, and as so modified be further studied.

(8) That the distillation method as described on page 172 be adopted as an official method for the determination of total arsenic in calcium arsenate.

(9) That recommendation (6) of this report apply equally to calcium arsenate.

(10) That the distillation method as described on page 175 be adopted as official for the determination of total arsenic in zinc arsenite.

(11) That Method II, page 175, for the determination of total arsenic in zinc arsenite be discarded.

(12) That recommendation (3) apply equally to zinc arsenite.

(13) That recommendation (6) apply equally to zinc arsenite.

(14) That Methods I and II for the determination of zinc oxid in zinc arsenite be further studied.

(15) That method (b) for the determination of moisture in Bordeaux mixture, Bordeaux-Paris green, and Bordeaux-lead arsenate mixtures, when in the form of pastes, as described on page 178 be adopted as official.

(16) That the method for the determination of carbon dioxid in Bordeaux mixture, Bordeaux-Paris green, and Bordeaux-lead arsenate, as described on page 178 be adopted as official.

(17) That the electrolytic method for the determination of copper in Bordeaux mixture as described on page 178 be adopted as an official method.

(18) That the thiosulphate titration method for the determination of copper in Bordeaux mixture as described on page 178 be adopted as an official method.

(19) That the method for water-soluble arsenious oxid in Bordeaux-Paris green as described on pages 179–180 be changed so as to require carbon-dioxid-free water and as so changed be adopted as a tentative method.

(20) That the distillation method for the determination of total arsenic in Bordeaux-Paris green as described on page 179 be adopted as an official method.

(21) That recommendation (3) of this report apply equally to Bordeaux-Paris green.

(22) That the electrolytic method for the determination of copper in Bordeaux-lead arsenate as described on page 182 be studied further with reference to its applicability to the determination of copper in both Bordeaux-Paris green and Bordeaux-lead arsenate, particular attention to be given to the effect of the various impurities which may be present in commercial samples.

(23) That the thiosulphate titration method for the determination of copper in Bordeaux-Paris green as described on page 178 be further studied.

(24) That the method for water-soluble arsenic oxid in Bordeaux-lead arsenate as described on page 182 be adopted as a tentative method.

(25) That the method for the determination of lead oxid in Bordeaux-lead arsenate as described on page 182 be further studied.

(26) That the silicotungstic-acid method for the determination of nicotin as described on page 183 be adopted as an official method.

(27) That the coöperative work on insecticides for next year include a study of the following:

(a) A method other than an electrolytic one for the separation and determination of copper and lead in a Bordeaux-lead arsenate mixture.

(b) Methods for the determination of the principal ingredients in zinc-arsenic compounds, alone and in combination with Bordeaux mixture.

The association adjourned at 12.30 p. m., to reassemble at 1.30 p.m.

PROCEEDINGS OF THE THIRTY-SECOND ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1915.

THIRD DAY.

WEDNESDAY—AFTERNOON SESSION.

REPORT OF COMMITTEE ON NOMINATIONS.

By W. B. Ellett (Agricultural Experiment Station, Blacksburg, Va.), *Chairman.*

The committee submitted the following nominations for officers for the year ending November, 1916: president, R. N. Brackett, of South Carolina; vice-president, J. K. Haywood, of Washington, D. C.; secretary-treasurer, C. L. Alsberg, of Washington, D. C.; additional members of the executive committee, W. J. Jones, jr., of Indiana, and E. B. Holland, of Massachusetts.

The secretary was instructed to cast the unanimous ballot of the association for these officers.

REPORT OF COMMITTEE ON RESOLUTIONS.

By R. J. Davidson (Polytechnic Institute, Blacksburg, Va.), *Chairman.*

Resolved, That the cordial thanks of this association be extended to our secretary, C. L. Alsberg, the executive committee, and the publishers, the Williams & Wilkins Company, of Baltimore, for the culmination of their efforts which has resulted in the successful publication of the Journal of this association.

Resolved, That the hearty thanks of this association be extended to the committee on editing methods of analysis for the painstaking care with which this laborious and extensive work has been conducted and presented for publication.

Resolved, That the thanks of the association be extended to the Chemical Society of Washington for the entertainment on Tuesday, November 16, 1915.

Resolved, That this association extend cordial thanks to W. D. Bigelow and the National Canners Association for their hospitality.

Resolved, That this association express to the secretary's assistant, Miss N. A. Parkinson, its sincere appreciation for her valued assistance extended so charmingly to all of its members.

Resolved, That the thanks of this association be extended to the Raleigh Hotel for the use of the banquet hall and other conveniences and for the courtesies shown to the members of this association.

Resolved, That the association hereby expresses to President Jones its appreciation for his unfailing courtesy and impartiality in conducting the difficult affairs of his office.

The report of the committee was approved.

No report was made by the associate referee on nitrogenous compounds of soils.

REPORT OF COMMITTEE OF REVIEW ON THE ANALYSIS OF LIME SULPHUR SOLUTIONS.

By R. J. DAVIDSON (Polytechnic Institute, Blacksburg, Va.), *Chairman.*

It is recommended—

(1) That the present referee be requested to furnish the chairman of the committee on editing methods of analysis with some methods to be printed by that committee.

(2) That it would be wise to discontinue this committee and refer the work to the regular referee on this subject.

The recommendations were approved.

No report was made by the referee on medicinal plants and drugs.

No report was made by the associate referees on synthetic products, medicated soft drinks, and medicinal plants.

REPORT ON ALKALOIDS.

By H. C. FULLER (Institute of Industrial Research, Washington, D. C.), *Associate Referee.*

The general plan of study adopted involves the determination of certain of the alkaloids which are commonly found in preparations in general use among physicians and which are made in a very large way by the manufacturing pharmacist. It was decided that strychnin should be the first alkaloid considered.

Three samples were examined: (1) A carefully prepared mixture of strychnin sulphate and milk sugar; (2) a sample of carefully prepared tablets containing 0.1 grain of strychnin sulphate; and (3) a sample of carefully made tablets containing 0.01 grain of strychnin sulphate. Two methods were used.

INSTRUCTIONS TO COLLABORATORS.

Employ both Methods I and II for determining the strychnin sulphate in Samples 1, 2, and 3. Take 0.3000 gram of Sample 1. Take 10 tablets of Sample 2, weighing carefully. Take 25 tablets of Sample 3, weighing carefully.

Report results as follows: Percentage of strychnin and strychnin sulphate in all three samples; grains of strychnin sulphate per tablet in Samples 2 and 3.

Method I.

Transfer a carefully weighed amount, 0.3000 gram, of the powder to a 200 cc. Squibb separator and moisten with 5 cc. of water. Add 1 cc. of stronger ammonia water. Agitate with 25 cc. of chloroform and allow to stand until separation is complete. Draw off the chloroform into a second separator and repeat the agitation twice with 25 cc. portions of the solvent. After combining all of the fractions, wash the combined chloroformic solutions by agitation with 10 cc. of water and allow to stand 15 minutes. Introduce a pledget of absorbent cotton into the stem of the separator and run off the chloroform into a tared dish, but do not allow the wash water to enter the orifice of the stop-cock. Add 10 cc. of chloroform, and when the water has entirely risen to the surface, run off the chloroform into the tared beaker. Wash off the outer surface of the stem of the separator with a little chloroform and then evaporate over a steam water bath, using a fan or blower and removing from the bath as the last portions evaporate to avoid decrepitation. Dry at 100°C. to a constant weight and weigh as strychnin. Check the weight of strychnin by dissolving the residue in neutral alcohol, adding an excess of N/10 sulphuric acid and titrating back with N/50 potassium hydroxid.

Strychnin to strychnin sulphate 1.2814, according to U.S.P.

One cubic centimeter of N/10 sulphuric acid is equivalent to 0.0334 gram of strychnin and 0.0428 gram of strychnin sulphate.

Method II.

Follow the procedure of Method I down to, but not including, the washing of the combined chloroform extract with water. Discard the alkaline solution remaining in the first separator. Treat the combined chloroform extracts with 10 cc. of N/1 sulphuric acid and agitate. Allow to stand until separation is complete and collect the chloroform in a second separator. Repeat the extraction with N/1 sulphuric acid twice more, discard the chloroform, and combine the acid fractions. Add stronger ammonia in excess, cool, and shake out with three successive portions of 25 cc. each of chloroform, finally combining all fractions. Wash the combined chloroform solutions by agitation with 10 cc. of water and allow to stand 15 minutes. Draw off the solvent through a pledget of absorbent cotton into a tared dish and finish the determination precisely as described in Method I.

TABLE 1.

Cooperative results on Sample 1.

(Containing 17.76 per cent of strychnin sulphate and 82.24 per cent of milk sugar.)

ANALYST	STRYCHNIN ALKALOID BY WEIGHT	STRYCHNIN SULPHATE BY WEIGHT	STRYCHNIN ALKALOID VOLUMETRIC	STRYCHNIN SULPHATE VOLUMETRIC
	METHOD I.			
	per cent	*per cent*	*per cent*	*per cent*
B. H. St. John, Wm. B. Warner Co., St. Louis, Mo.	14.10	18.07	12.93	16.57
C. K. Glycart, U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.	14.30 13.90	18.32 17.81	11.44 11.32	14.66 14.49
F. W. Heyl, Upton Chemical Co., Kalamazoo, Mich.	14.93	19.13	.....	17.12
C. H. Briggs, Institute of Industrial Research, Washington, D. C.	14.53 14.50	18.62 18.58	13.50 13.72	17.30 17.58
J. B. Luther, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	14.33	18.36	.....	.....
H. B. Mead, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	14.07	18.04	13.50	17.1
E. M. Bailey, Agricultural Experiment Station, New Haven, Conn.	14.45	18.52	14.00	17.92
H. C. Fuller, Institute of Industrial Research, Washington, D. C.	14.51	18.59	.....	.....
Average	14.36	18.40	12.91	16.59
	METHOD II.			
B. H. St. John	14.57	18.66	13.60	17.42
C. K. Glycart	14.26 13.77	18.26 17.64	12.54	16.07 .....
F. W. Heyl	15.1	19.13	.....	17.26
C. H. Briggs	14.50 14.40	18.58 18.45	13.72	17.58 .....
J. B. Luther	14.50	18.58	.....	.....
H. B. Mead	14.40	18.45	13.0	16.66
E. M. Bailey	14.43	18.49	14.03	17.95
H. C. Fuller	13.83	17.72	.....	.....
Average	14.37	18.39	13.37	17.14

TABLE 2.

Cooperative results on Sample 2.

(Strychnin sulphate—1/10 grain tablet.)

ANALYST	STRYCHNIN ALKALOID BY WEIGHT	STRYCHNIN SULPHATE BY WEIGHT		STRYCHNIN ALKALOID BY TITRATION	STRYCHNIN SULPHATE BT TITRATION	
				METHOD I.		
	per cent	*per cent*	*grain per tablet*	*per cent*	*per cent*	*grain per tablet*
B. H. St. John	7.54	9.80	0.1004	7.08	9.05	0.093
C. K. Glycart	7.58	9.71	0.099	6.47	8.28	0.085
	7.31	9.37	0.096	6.50	8.32	0.087
F. W. Heyl	8.34	10.50	0.096	.....	9.77	.....
	8.26	.....	.....	.....	9.33	.....
	8.19	.....	.....	.....	9.48	.....
C. H. Briggs	7.77	9.95	0.1028	7.34	9.40	0.097
	7.87	10.09	0.1048	7.30	9.35	0.097
J. B. Luther	7.55	9.67	0.0978	.....	.....	.....
H. B. Mead	7.54	9.66	.....	7.07	9.06	.....
E. M. Bailey	7.81	10.01	0.103	7.59	.....	.....
H. C. Fuller	7.64	9.78	0.103	7.22	9.25	0.097
Average	7.78	9.85	0.1003	7.07	9.13	0.092
				METHOD II.		
B. H. St. John	7.45	9.55	0.1000	7.04	9.03	0.0942
C. K. Glycart	7.24	9.27	0.096	6.49	8.31	0.086
	6.91	8.84	0.092	6.49	8.31	0.087
F. W. Heyl	8.41	10.70	0.092	.....	9.46	.....
C. H. Briggs	7.77	9.56	0.1028	7.34	9.40	0.09716
	7.93	10.16	0.1058	7.30	9.35	0.09716
J. B. Luther	7.76	9.94	0.0978	.....	.....	.....
H. B. Mead	7.55	9.67	.....	7.10	9.10	.....
E. M. Bailey	7.67	9.83	0.101	7.23	.....	.....
H. C. Fuller	7.61	9.75	0.099	6.23	7.99	0.082
Average	7.63	9.72	0.098	6.99	8.95	0.090

TABLE 3.

Cooperative results on Sample 2.

(Strychnin sulphate—1/100 grain tablet.)

ANALYST	STRYCHNIN ALKALOID BY WEIGHT	STRYCHNIN SUPLHATE BY WEIGHT		STRYCHNIN ALKALOID VOLUMETRIC	STRYCHNIN SULPHATE VOLUMETRIC	
			METHOD I.			
	per cent	*per cent*	*grain per tablet*	*per cent*	*per cent*	*grain per tablet*
B. H. St. John .	0.84	1.08	0.0110	0.72	0.93	0.0095
C. K. Glycart. .	0.76	0.97	0.01	0.62	0.80	0.008
	0.78	1.00	.....	0.63	0.80	.....
F. W. Heyl....	0.90	1.21	0.012	....	0.98	0.0099
	0.99	....	.....	....	....	.....
C. H. Briggs...	1.00	1.28	0.012	0.77	0.99	0.0099
	0.84	1.08	0.015	0.76	0.97	.....
J. B. Luther ...	0.87	1.12	0.011	....	....	.....
H. B. Mead....	0.91	1.17	.....	0.62	0.81	.....
E. M. Bailey...	0.88	1.18	0.011	0.86	....	.....
H. C. Fuller....	0.84	1.07	0.0106	.....	....	.....
Average.....	0.87	1.12	0.011	0.71	0.91	0.0093
			METHOD II.			
B. H. St. John .	0.86	1.10	0.0110	0.68	0.87	0.0095
C. K. Glycart. .	0.74	0.95	0.01	0.62	0.80	0.008
	0.75	0.97	.....	0.62	0.80	.....
F. W. Heyl....	1.07	1.37	0.013	....	0.98	0.0098
C. H. Briggs...	0.87	1.11	0.011	0.77	0.99	0.0099
	0.84	1.08	.....	0.76	0.97	.....
J. B. Luther...	0.82	1.07	0.010	....	....	.....
H. B. Mead ...	0.85	1.09	.....	0.61	0.71	.....
E. M. Bailey...	0.84	1.08	0.011	0.82	....	.....
H. C. Fuller....	0.82	1.06	0.010	0.86	1.09	0.010
Average.....	0.85	1.09	0.012	0.73	0.91	0.0094

CONCLUSIONS.

It is evident from a study of the above figures that the determination of strychnin by titration can not be recommended.

Average results indicate that there is no advantage in using the second method, which considerably lengthens the determination. Individual results, however, indicate that there is some advantage in using Method II.

It is recommended that in conducting assays for strychnin, reliance be placed on a gravimetric determination and not on a determination obtained by volumetric means. It is recommended, further, that another year be devoted to the study of methods for determining strychnin in tablets, with a view to incorporating further details which may improve the description of the process in such a way that individuals will be able to obtain more concordant results; and, furthermore, that the study of the determination of strychnin be extended to more complex mixtures.

DELICATE TEST FOR STRYCHNIN[1].

By H. E. Buc (Bureau of Chemistry, Washington, D. C.).

PREPARATION OF ZINC.

Treat granular zinc with a little concentrated hydrochloric acid so as to clear the surface. Pour off the acid. Cover the metal with 1% tartar emetic, shaking occasionally during 1 hour. Add a saturated solution of mercuric chlorid (1 cc. for every gram of zinc). Add a few drops of concentrated hydrochloric acid. After 30 minutes pour off the solution and wash thoroughly; dry.

TEST.

To the dry extracted alkaloid, or any of its salts, or to the aqueous solution, the volume of which is to be about 0.5 cc. or less, add 0.5–1 gram of the zinc amalgam and 0.5 cc. of concentrated hydrochloric acid. If the amount of strychnin is very small (less than 0.01 mg.), allow to stand 15 or 20 minutes. With larger quantities much less time is required. (To save time, after about 2 minutes test a few drops and, if negative, allow to stand full time.) Pour off the solution from the zinc, taking care not to carry along any zinc particles. Add by drops a 0.02% solution of potassium ferricyanid (K_3FeCy_6). A pink to rose red coloration indicates strychnin.

Large amounts of some alkaloids and other organic substances interfere by reacting with ferricyanid ($K_3Fe_9(CN)_6$).

In the absence of interfering substances this test will indicate about 0.001 mg. of strychnin.

H. E. Buc (Bureau of Chemistry, Washington, D. C.), submitted a paper on "The Estimation of Strychnin in Presence of Quinin."

[1] Modification of Malaquin's test.

PRELIMINARY STUDY OF SOME OF THE PHYSICAL AND CHEMICAL CONSTANTS OF BALSAM PERU.

By E. C. MERRILL[1] (U. S. Bureau of Chemistry, Washington, D. C.),
Associate Referee on Balsams and Gum Resins.

A preliminary study of the method for the determination of the iodin value of the cinnamein of Peru balsam was conducted. Some physical constants, such as viscosity, surface tension, optical rotation, and refractometer readings, were also studied superficially.

IODIN VALUE OF CINNAMEIN[2].

Obtain cinnamein from Peru balsam by shaking out the ethereal solution of the balsam with 2 or 3 successive portions of 5% potassium hydroxid in the same manner as in determining the unsaponifiable material in a soap. Wash the ethereal solution once or twice with 10 mils of water and filter through cotton, drive off the ether, and dry the cinnamein in vacuum desiccator over sulphuric acid for about 12 hours. Take about 1 gram of the dried cinnamein for the iodin value, weigh into a glass capsule, transfer to an iodin number bottle, add 10 mils of chloroform and 30 mils of Hanus solution. After standing 30 minutes add 100 mils of water, followed by 10 mils of 15% potassium iodid solution, and excess of iodin titrated with thiosulphate in the usual manner, using starch indicator when near the end point. Carry out a control, using the above stated amounts of reagents and same time for reactions.

Results on artificial and true Peru balsam.

SAMPLE	DESCRIPTION	IODIN NUMBER (HANUS)	IODIN NUMBER (WIJS)	PERCENTAGE INCREASE, WIJS OVER HANUS
A	Labeled synthetic Peru balsam	39.47	49.34	25
B	Presumably true	22.07	42.64	73
C	Presumably true	26.53	39.25	32
D	Presumably true	25.96	38.34	49
E	Reported as synthetic	4.70	3.9	..
F	Reported as adulterated	21.53	31.25	45
G	Known to be artificial[a]	26.51	32.80	23

[a] Sample from W. O. Emery. Obtained from a German manufacturer.

The same quantity of Wijs' solution and other reagents was used in the Wijs as in the Hanus method. The results on these two methods suggest the need of further investigation of the Hanus method before submitting for collaboration.

INFLUENCE OF AGE OR EXPOSURE TO AIR ON IODIN VALUE.

The following table indicates the influence of age or exposure to air on the iodin number of cinnamein in balsam Peru. Column 3 shows the

[1] Present address, United Drug Company, Boston, Mass.
[2] Method as at present employed.

influence of treating the balsam with a current of air for 24 hours and Column 4 of shaking the balsam with hydrogen peroxid for 24 hours previous to extraction of cinnamein.

Results when subjected to oxidizing influences.

SAMPLE	IODIN NUMBER (WIJS)	IODIN NUMBER (WIJS) AFTER TREATMENT WITH AIR CURRENT	IODIN NUMBER (WIJS) AFTER TREATMENT WITH HYDROGEN PEROXID
A	49.34	44.67	45.13
B	42.64	32.63	32.64
C	39.25	36.28	38.50
D	38.34	36.67	35.51
E	3.90	1.60	3.20

INFLUENCE OF TIME ON IODIN VALUE.

The time factor for absorption of iodin by Hanus solution has been investigated. Results indicate that the time at present employed (30 minutes) is insufficient for complete absorption.

Results showing influence of time on absorption of iodin.

TIME	IODIN VALUE
15 minutes	17.70
30 minutes	22.37
1 hour	23.34
2 hours	23.80
3 hours	27.36
4 hours	27.00

VISCOSITY OF PERU BALSAM.

No marked difference in viscosity between true and artificial Peru balsam was noted. The following table gives a measure of relative viscosity on the samples studied.

Comparative table showing time of efflux.

SAMPLE	TIME
	seconds
A[a]	31.4
B	90.0
C	154.2
D	94.6
E	88.0
F[a]	112.0
G[a]	28.0

[a] Artificial.

SURFACE TENSION OF BALSAM PERU.

The relative surface tension of the above samples was estimated by means of the ordinary stalagmometer. Since the surface tension is proportional to the drop weight, results are reported as drop weights in milligrams compared with water.

Results showing surface tension values.

SAMPLE	WEIGHT OF DROP	COMPARED WITH WATER AT 25°
	mg.	
A[a]	35.6	0.283
B	42.6	0.338
C	41.3	0.329
D	42.7	0.339
E[a]	44.6	0.354
F[a]	48.3	0.383
G[a]	39.9	0.317
Water at 25°	125.8	1.000

[a] Artificial.

There appears to be a general digression in the values for genuine as compared with artificial balsams. While the results obtained are not conclusive on account of the limited number of samples studied, they indicate the possibility of the surface tension value being useful as a factor in connection with the other constants of Peru balsams.

OPTICAL ROTATION OF CINNAMEIN IN SOLUTION.

The optical rotation of solution of cinnamein in benzol was determined. Solutions containing 2 cc. of cinnamein in 10 cc. of benzol were polarized in 100 mm. tubes.

Polarization in angular degrees at 25°C.

SAMPLE	ROTATION
A[a]	+ 0.35
B	0
C	+ 0.10
D	0
E[a]	+ 0.35
F[a]	+ 0.17
G[a]	No reading

[a] Artificial.

The cinnamein obtained from the artificial product appears to give a slight dextrorotation, which is also noted to a lesser extent in one of the samples reported as genuine. The cinnamein of pure Peru balsam shows little or no rotation.

REFRACTOMETER READINGS OF CINNAMEIN.

In the case of the artificial Peru balsams, the refractive index of the cinnamein is lower than 1.57; in the natural Perus the figure is above 1.57. This factor may prove useful in the final consideration of the constants of Peru balsam.

Refractometer readings.

SAMPLE	READINGS AT 25°C.
A[a]	1.5450
B	1.5765
C	1.5710
D	1.5720
E[a]	1.5635
F[a]	1.5665
G[a]	1.5692

[a] Artificial.

CONCLUSIONS.

(1) The method for determination of iodin value of cinnamein by Hanus method as at present employed is unsatisfactory and, furthermore, may be entirely inadequate as an index of the character of pure Peru balsam.

(2) The employment of such physical constants as the viscosity, surface tension, optical rotation, and refractometer observation may prove of value in the final interpretation of the character of Peru balsams.

RECOMMENDATIONS.

It is recommended—

(1) That further investigation be made, along the lines above indicated, upon a large number of samples during the coming year.

(2) That, if a satisfactory method for determination of iodin value for Peru balsam be developed within the coming year, the same be presented for collaboration.

At the request of the committee on editing methods of analysis, a paper on the "Determination of Pepsin in Liquids" was presented by V. K. Chesnut (Bureau of Chemistry, Washington, D. C.), *Associate Referee*, but is not reprinted here, as practically the same material has been printed elsewhere[1].

W. S. Hubbard[2] (Bureau of Chemistry, Washington, D. C.), submitted a paper on the "Identification of Emodin-Bearing Drugs".

B. H. St. John[3] (Bureau of Chemistry, Washington, D. C.), submitted a paper on "Alcohol Tables"[4].

[1] U. S. Bur. Chem. *Bull.* 162, 210–1.
[2] Present address, Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.
[3] Present address, Wm. R. Warner and Company, St. Louis, Mo.
[4] *J. Assoc. Official Agr. Chemists*, 1916, 2: No. 2 (II), 208–35.

REPORT OF COMMITTEE TO COOPERATE WITH OTHER COMMITTEES ON FOOD DEFINITIONS AND STANDARDS.

By WILLIAM FREAR (Agricultural Experiment Station, State College, Pa.), *Chairman.*

The committee appointed to cooperate with other committees from the Association of American Dairy, Food and Drug Officials and from the U. S. Department of Agriculture to formulate definitions and standards for the guidance of this association in the enforcement of food, drug, and sanitary laws submits the following report of progress:

Supplementary to the very brief report made at the 1914 meeting of this association[1], the following actions taken by the joint committee on definitions and standards should be mentioned:

ORGANIZATION OF THE COMMITTEE.

CHAIRMAN.....Carl L. Alsberg, Bureau of Chemistry, Washington, D. C.
SECRETARY.....J. S. Abbott, Bureau of Chemistry, Washington, D. C.
ASSISTANT SECRETARY....P. B. Dunbar, Bureau of Chemistry, Washington, D. C.

MEMBERSHIP.

U. S. Department of Agriculture:
Carl L. Alsberg, Robert L. Emerson, Isaac K. Phelps, all of Washington, D. C.

Association of American Dairy, Food and Drug Officials:
E. F. Ladd, of North Dakota; W. F. Hand, of Mississippi; H. E. Barnard, of Indiana.

Association of Official Agricultural Chemists:
Wm. Frear, of Pennsylvania; J. P. Street, of Connecticut; Julius Hortvet, of Minnesota.

RESOLUTIONS ADOPTED BY THE COMMITTEE.

(1) That the subject matter for the consideration of the committee should include all materials coming within the scope of the Food and Drugs Act, or the food, drug, and sanitary laws of the various States.

(2) That for the purpose of expediting the work of the standards committee each member thereof be made a subcommittee in charge of a subject or group of subjects that will be assigned, and have power to appoint collaborators from the U. S. Department of Agriculture, the Association of Official Agricultural Chemists, the Association of American Dairy, Food and Drug Officials, or other official departments.

(3) That for the unification and further expedition of the work, an advisory committee of three be appointed to cooperate with the various subcommittees with a view to correcting the work of these subcommittees. It is also suggested that the primary plans of the subcommittees be submitted to the advisory committee for review and consideration; also that preliminary reports be submitted to the advisory committee for consideration so that subjects requiring final action by the entire committee may be simplified as far as possible.

---

[1] *J. Assoc. Official Agr. Chemists*, 1915, **1**: 462.

The advisory committee appointed under this resolution was Messrs. Alsberg, Frear and Ladd.

PRINCIPLES OF STANDARDIZATION.

The following principles have been adopted by the joint committee:

(1) The standards are expressed in the form of definitions, with or without accompanying specifications of quality or composition.

(2) In formulating new standards the joint committee will in each case refer back to the underlying standard promulgated in Circular 19, Office of the Secretary, U. S. Department of Agriculture, stating specifically that it is either accepted or modified, and stating the modification.

(3) The definitions are so formed as to exclude from the articles defined substances not included in the definitions.

(4) A term defined in any of the several schedules has the same meaning wherever else it is used in this report.

(5) The names of food products herein defined preferably agree with existing American usage as known to the consumer.

PROCEDURE FOR THE ADOPTION OF STANDARDS.

It was resolved that—

"The general policy of the committee in adopting standards shall be as follows: After the committee has agreed, the proposed standards shall be recommended to the Association of American Dairy, Food and Drug Officials by its representatives. In the event of favorable action by that association, they shall be presented to the Association of Official Agricultural Chemists. In the event of favorable action by the Association of Official Agricultural Chemists, they shall be recommended to the Secretary of Agriculture for publication by the department.

"Any three members reporting to their organization shall make their recommendation for the adoption of standards subject to ratification by the other organizations, but this procedure, *i. e.*, ratification by the entire association, may be ignored in emergency cases by the various executives concerned."

SUBJECTS CHOSEN FOR IMMEDIATE CONSIDERATION.

The committee decided to consider first those questions now most urgently requiring determination.

Flour and meal, exclusive of feed	Ladd.
Fruit juices and soda flavors	Hand.
Soft drinks, orangeade powder, temperance beverages	Hand.
Condensed milk	Hortvet.
Dried milk, whole milk powder	Hortvet.
Cocoa and chocolate	Hortvet.
Edible cereal pastes	Emerson.
Canned goods	Frear.
Toxicity (among metals)	Alsberg.
Dried fruits	Barnard.
Hydrogenated fats, oils	Barnard.
Candy	Phelps.

Marmalades, sirups, jams	Phelps.
Pharmaceuticals (cod liver oil emulsion, colocynth, laudanum, saccharine tablets, hypophosphites, tr. nux vomica, asafetida)	Street.
Pepper, spices, including herbs used for spices	Street.
Vinegar	Street.
Manufactured egg products	Emerson.
Baking powder, flavoring materials	Hand.

Other subjects upon which immediate study was determined to be desirable but which have not yet been specifically assigned are:

Molasses and honeys.	Edible oils and fats.
Butter.	Meat and plant extracts.
Cream.	Breakfast foods.
Cheese.	Disinfectants.
Ice cream.	Beef, iron, and wine.
Ices and frozen custards.	Pepsin-pancreatin.

MEETINGS AND HEARINGS.

The committee has met in the performance of its duties as follows:

April 13-14, 1914, at Washington, D. C.
July, 1914, at Portland, Me.
November, 1914, at Washington, D. C.
April, 1915, at Washington, D. C.
June, 1915, at Washington, D. C.

The following hearings have been held:

Condensed milk, conducted by J. S. Abbott, Chicago, September 8, 1914.
Gluten flour and diabetic foods, by J. P. Street, New York, January 25, 1915.
Flour and cereal products, by E. F. Ladd, Chicago, May 3, 1915.
Macaroni and spaghetti, by R. L. Emerson, Washington, D. C., May 14, 1915.
Flour, by the joint committee, Washington, D. C., June 5, 1915.

Stenographic reports of these hearings were promptly supplied to all committee members for study.

GRADES FOR FOODSTUFFS.

In addition to the matters above set forth, the committee has been considering carefully the subject of standards for food grades, with the purpose of supplementing the existing system of minimum standards with standards for the related grades, wherever this is desirable and practicable.

The representatives of this association on the joint committee now have to report, with a recommendation that you formally ratify them, the following definitions and standards, which have been adopted by the joint committee and ratified August 3, 1915, by the Association of American Dairy, Food and Drug Officials:

CORN.

By virtue of the authority vested in the Secretary of Agriculture by the acts of Congress of June 30, 1906[1], and of March 4, 1913[2], to fix definite grades of grain, the following grades for corn are hereby fixed and promulgated, to take effect on July 1, 1914:

Grades for commercial corn.

GRADE CLASSIFICATION (WHITE, YELLOW, AND MIXED CORN)	MAXIMUM PERCENTAGES OF—			
	MOISTURE	DAMAGED CORN	FOREIGN MATERIAL, INCLUDING DIRT, COB, OTHER GRAINS, FINELY BROKEN CORN, ETC.	"CRACKED" CORN, NOT INCLUDING FINELY BROKEN CORN. (SEE GENERAL RULE NO. 9)
No. 1	14.0	2 Exclusive of heat-damaged or mahogany kernels	1	2
No. 2	15.5	4	1	3
No. 3	17.5	6	2	4
No. 4	19.5	8 May include heat-damaged or mahogany kernels not to exceed— 0.5%	2	4
No. 5	21.5	10 1%	3	5
No. 6	23.0	15 3%	5	7
"Sample"	See General Rule No. 6 for "sample" grade.			

GENERAL RULES.

(1) The corn in grades No. 1 to No. 5, inclusive, must be sweet.

(2) *White corn*, all grades, shall be at least 98 per cent (98%) white.

(3) *Yellow corn*, all grades, shall be at least 95 per cent (95%) yellow.

(4) *Mixed corn*, all grades, shall include corn of various colors not coming within the limits for color as provided under white or yellow corn.

(5) In addition to the various limits indicated, No. 6 corn may be musty, sour, and may also include corn of inferior quality, such as immature and badly blistered.

(6) All corn that does not meet the requirements of either of the six (6) numerical grades by reason of an excessive percentage of moisture, damaged kernels, foreign matter, or "cracked" corn, or corn that is hot, heat damaged, fire burnt, infested with live weevils, or otherwise of distinctly low quality shall be classed as "sample" grade.

(7) In No. 6 and "sample" grade, reasons for so grading shall be stated on the inspector's certificate.

(8) *Finely broken corn* shall include all broken particles of corn that will pass through a perforated metal sieve with round holes nine sixty-fourths ($\frac{9}{64}$) of an inch in diameter.

(9) *"Cracked" corn* shall include all coarsely broken pieces of kernels that will pass through a perforated metal sieve with round holes one-quarter ($\frac{1}{4}$) of an inch in diameter, except that the finely broken corn, as provided for under Rule No. 8, shall not be considered as "cracked" corn.

(10) It is understood that the damaged corn; the foreign material, including pieces of cob, dirt, finely broken corn, other grains, etc.; and the coarsely broken or "cracked"

[1] U. S. Statutes at Large, 1905-7, **34**: Pt. I, 686.
[2] Ibid., 1911-3, **37**: Pt. I, 835.

corn, as provided for under the various grades, shall be such as occur naturally in corn when handled under good commercial conditions.

(11) Moisture percentages, as provided for in these grade specifications, shall conform to results obtained by the standard method and tester[1].

CACAO PRODUCTS.

Cacao beans, cocoa beans, are the seeds of the cacao tree, *Theobroma cacao L.*

Cacao nibs, cocoa nibs, cracked cocoa, is the roasted, broken cacao bean freed from its shell or husk.

Chocolate, plain chocolate, bitter chocolate, chocolate liquor, chocolate paste, bitter chocolate coatings, is the solid or plastic mass obtained by grinding cacao nibs without the removal of fat or other constituents except the germ.

Chocolate, plain chocolate, bitter chocolate, chocolate liquor, chocolate paste, bitter chocolate coatings, contains not more than three per cent (3%) of ash insoluble in water, three and fifty hundredths per cent (3.50%) of crude fiber, nine per cent (9%) of cacao starch, and not less than forty-five per cent (45%) of cacao fat.

Sweet chocolate, sweet chocolate coatings, is chocolate mixed with sugar (sucrose), with or without the addition of cocoa butter, spices, or other flavoring materials.

Sweet chocolate, sweet chocolate coatings, contains in the sugar- and fat-free residue no higher percentage of ash, fiber or starch than is found in the sugar- and fat-free residue of chocolate.

Cocoa, powdered cocoa, is cacao nibs, with or without the germ, deprived of a portion of its fat and finely pulverized.

Cocoa, powdered cocoa, contains percentages of ash, crude fiber and starch corresponding to those in chocolate after correction for fat removed.

Sweet cocoa, sweetened cocoa, is cocoa mixed with not more than sixty per cent (60%) of sugar (sucrose).

Sweet cocoa, sweetened cocoa, contains in the sugar- and fat-free residue no higher percentage of ash, crude fiber or starch than is found in the sugar- and fat-free residue of chocolate.

Milk chocolate, milk cocoa, sweet milk chocolate or sweet milk cocoa, respectively, is chocolate, cocoa, sweet chocolate or sweet cocoa which contains not less than twelve per cent (12%) of whole milk solids in the finished product.

GLUTEN PRODUCTS AND "DIABETIC" FOOD.

Ground gluten is the clean, sound product made from wheat flour by the almost complete removal of starch and contains not more than ten per cent (10%) of moisture, and, calculated on the water-free basis, not less than fourteen and two-tenths per cent (14.2%) of nitrogen, not more than fifteen per cent (15%) of nitrogen-free extract (using the protein factor 5.7), and not more than five and five-tenths per cent (5.5%) of starch (as determined by the diastase method).

Gluten flour is the clean, sound product made from wheat flour by the removal of a large part of the starch and contains not more than ten per cent (10%) of moisture, and, calculated on the water-free basis, not less than seven and one-tenth per cent (7.1%) of nitrogen, not more than fifty-six per cent (56%) of nitrogen-free extract (using the protein factor 5.7), and not more than forty-four per cent (44%) of starch (as determined by the diastase method).

Gluten flour, self-raising, is a gluten flour containing not more than ten per cent (10%) of moisture, and leavening agents with or without salt.

---

[1] U. S. Bur. Plant Ind. *Circ.* 72, 1–16.

"Diabetic" food. Although most foods may be suitable under certain conditions for the use of persons suffering from diabetes, the term "diabetic" as applied to food indicates a considerable lessening of the carbohydrates found in ordinary products of the same class, and this belief is fostered by many manufacturers on their labels and in their advertising literature.

A "diabetic" food contains not more than half as much glycogenic carbohydrates as the normal food of the same class. Any statement on the label which gives the impression that any single food in unlimited quantity is suitable for the diabetic patient is false and misleading.

EGG NOODLES AND PLAIN NOODLES.

Noodles, egg noodles, are dried alimentary pastes made from wheat flour and egg. They contain not less than five per cent (5%) by weight of the solids of whole, sound egg exclusive of the shell.

Plain noodles, water noodles, are dried alimentary pastes made from wheat flour without egg, or with less than five per cent (5%) by weight of the solids of whole, sound egg exclusive of the shell.

Standards for moisture in these products are under consideration.

CONDENSED MILK, EVAPORATED MILK, CONCENTRATED MILK.

Condensed milk, evaporated milk, concentrated milk, is the product resulting from the evaporation of a considerable portion of the water from the whole, fresh, clean, lacteal secretion obtained by the complete milking of one or more healthy cows, properly fed and kept, excluding that obtained within fifteen (15) days before and ten (10) days after calving, and contains, all tolerances being allowed for, not less than twenty-five and five-tenths per cent (25.5%) of total solids and not less than seven and eight-tenths per cent (7.8%) of milk fat.

MAPLE PRODUCTS.

Maple sugar, maple concrete, is the solid product resulting from the evaporation of maple sap or maple sirup.

Maple sirup is sirup made by the evaporation of maple sap or by the solution of maple concrete, and contains not more than thirty-five per cent (35%) of water and weighs not less than eleven (11) pounds to the gallon (231 cu. in.).

MACARONI, SPAGHETTI, VERMICELLI, AND SIMILAR ALIMENTARY PASTES.

Definition and standard adopted by the joint committee on definitions and standards, June 4, 1915:

Macaroni, spaghetti, vermicelli, and similar alimentary pastes, are dried alimentary pastes made from the semolina of hard wheat.

Products made in the shape of macaroni, spaghetti, vermicelli, and similar alimentary pastes from material other than the semolina of hard wheat are imitations.

A standard for moisture in these products is under consideration.

A paper on the "Proposed Committee on Bacteriological Examination of Foodstuffs" was presented by Charles Thom (Bureau of Chemistry, Washington, D. C.).

The appointment of such a committee was referred, by vote of the association, to the executive committee.

INORGANIC PHOSPHORUS IN ANIMAL TISSUE.

By F. M. Beegle (Agricultural Experiment Station, Wooster, Ohio),
Referee on Organic and Inorganic Phosphorus in Foods, Feeding Stuffs and Drugs.

A critical study of some of the details in the method for inorganic phosphorus in animal tissue is outlined in this report. The details studied were: (1) The influence of hot ammonium sulphate on the water extract; (2) the effects of different amounts of magnesia-mixture in the first precipitation; and (3) the time required for complete precipitation of phosphorus in the presence of large amounts of ammonium sulphate.

All determinations were made in triplicate on samples of flesh, with and without the addition of known amounts of inorganic phosphates.

PREPARATION OF COLD WATER EXTRACT OF MUSCLE.

A. COLD WATER EXTRACT OF MUSCLE.

Weigh 10–12 grams of fresh muscle and divide as nearly equally as possible between 2 small beakers. Moisten the samples with a few cc. of water and break up lumps with a glass rod. Add 50 cc. of water to each beaker and stir the contents for 15 minutes. Allow the insoluble residue to settle for 3–5 minutes, then decant the liquid from each beaker through filters into beakers, allow to drain, and add 25 cc. of water. Stir for 7–8 minutes, allow to settle, and decant onto the same filter. Continue this treatment, using 25 cc. of water each time, until the filtrates measure about 230 cc. each. Allow the filters to drain completely between extractions. Whenever the major portion of the residue has become mechanically transferred to the filter, return it to the beaker, using great care not to break the filter paper. After the last extraction, throw the entire contents of each beaker onto the filter and, when drained, wash twice with small quantities of water. Combine the 2 extracts, and use for the precipitation of phosphates.

B. COLD WATER EXTRACT OF MUSCLE PLUS PHOSPHATE.

Weigh the same quantity of flesh as specified above, and divide as nearly equally as possible between 2 small beakers; work up with a few cc. of water; add 25 cc. of aqueous solution of disodium phosphate ($Na_2HPO_412H_2O$) equivalent to about 40 mg. of magnesium pyrophosphate, dividing as nearly equally as possible between the 2 beakers, and proceed as directed under (A). The extract thus obtained is ready for precipitation.

MAGNESIA-MIXTURE METHOD FOR THE DETERMINATION OF INORGANIC PHOSPHORUS IN EXTRACTS OF ANIMAL TISSUES.

Treat 3 of the extracts prepared according to (A) and 3 of those prepared according to (B) as follows:

Add 50 cc. of magnesia-mixture, stirring freely. Allow to stand 15 minutes, add 25 cc. of ammonia (sp. gr. 0.90), cover and allow to stand 3 days. On the morning of

the third day filter and wash the precipitate with 2.5% ammonia water. Dissolve the precipitate on the filter paper and that remaining in the beaker in which the precipitation was made with dilute nitric acid (1 : 1) and hot water, receiving the solution in 400 cc. beakers. Neutralize the nitric acid with ammonia; make slightly acid with nitric acid. Add 5 grams of ammonium nitrate and precipitate in the usual way with molybdate solution. Continue in the usual way for the gravimetric estimation of phosphorus as the pyrophosphate.

TABLE 1.

Test of magnesia-mixture method for inorganic phosphorus in flesh by recovery of added phosphates.

DETERMINATION	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE[a]	INORGANIC PHOSPHORUS	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	ADDED PHOSPHORUS RECOVERED AS MAGNESIUM PYROPHOSPHATE	
	grams	*gram*	*per cent*	*gram*	*gram*	*per cent*
Set A:						
No. 1	12.6221	0.0581	0.1282	.....	.....	.....
No. 2	8.1600	0.0370	0.1263	.....	.....	.....
No. 3	8.3565	0.0386	0.1287	.....	.....	.....
Average	.....	.....	0.1277	.....	.....	.....
No. 4	9.6914	0.1070	.....	.....	0.0626	.....
No. 5	8.0108	0.0995	.....	.....	0.0628	.....
No. 6	9.0040	0.1046	.....	.....	0.0632	.....
Average	.....	.....	.....	0.0624	0.0629	100.81
Set B:						
No. 7	9.6533	0.0436	0.1258	.....	.....	.....
No. 8	7.7024	0.0354	0.1281	.....	.....	.....
No. 9	12.4817	0.0569	0.1270	.....	.....	.....
Average	.....	.....	0.1270	.....	.....	.....
No. 10	9.2544	0.1061	.....	.....	0.0639	.....
No. 11	10.6438	0.1106	.....	.....	0.0621	.....
No. 12	10.9061	0.1118	.....	.....	0.0621	.....
Average	.....	.....	.....	0.0624	0.0627	100.48
Set C:						
No. 13	9.2229	0.0418	0.1263	.....	.....	.....
No. 14	11.1070	0.0509	0.1277	.....	.....	.....
No. 15	10.8454	0.0499	0.1282	.....	.....	.....
Average	.....	.....	0.1274	.....	.....	.....
No. 16	10.6190	0.1114	.....	.....	0.0628	.....
No. 17	11.5529	0.1141	.....	.....	0.0613	.....
No. 18	11.0007	0.1126	.....	.....	0.0623	.....
Average	.....	.....	.....	0.0624	0.0621	99.52

[a] All blanks deducted.

TABLE 2.

Test of the amount of time required for the complete precipitation of inorganic phosphates in the presence of large amounts of ammonium sulphate.

DETERMINATION	TIME OF STANDING	WEIGHT OF MAGNESIUM PYROPHOSPHATE RECOVERED	WEIGHT OF MAGNESIUM PYROPHOSPHATE ADDED	MAGNESIUM PYROPHOSPHATE RECOVERED
		gram	*gram*	*per cent*
Set A:				
No. 1	July 7—8	0.0616	.....	.....
No. 2	July 7—8	0.0622	.....	.....
No. 3	July 7—8	0.0619	.....	.....
Average	.....	0.0619	0.0624	99.18
Set B:				
No. 1	July 7—9	0.0645	.....	.....
No. 2	July 7—9	0.0613	.....	.....
No. 3	July 7—9	0.0625	.....	.....
Average	.....	0.0628	0.0624	100.64
Set C:				
No. 1	July 7—10	0.0627	.....	.....
No. 2	July 7—10	0.0627	.....	.....
No. 3	July 7—10	0.0620	.....	.....
Average	.....	0.0625	0.0624	100.16

DISCUSSION.

Determinations reported in Table 1 indicate that the magnesia-mixture method gives reliable results on flesh samples and complete recovery of added inorganic phosphates. The sample was extracted with $3\frac{1}{3}$ per cent ammonium sulphate in determinations 13 to 18 until the extract measured 450 cc. The extract was then cooled and precipitated according to the method described. Results obtained by both methods are practically identical, showing that hot $3\frac{1}{3}$ per cent ammonium sulphate does not affect the determination.

Set B was treated exactly the same as "A" except that 10 cc. instead of 50 cc. of the magnesia-mixture were used. The results compared with "A" are well within the limits of error, indicating that 10 cc. of magnesia-mixture are sufficient for complete precipitation in 10 to 12 gram samples of flesh.

Table 2 indicates the influence of time on complete precipitation in the presence of large amounts of ammonium sulphate. Equal amounts of inorganic phosphate solution of known strength were added to 500 cc. of $3\frac{1}{3}$ per cent ammonium sulphate, and then precipitated with 10 cc. of magnesia mixture. Set A stood 24 hours, Set B 48 hours, and Set C 72 hours before filtering. The phosphorus was then determined in the precipitate as usual. It is evident from a study of Table 2 that a greater time than 48 hours for precipitation makes very little difference in the average weights of the precipitates, and is unnecessary.

CONCLUSIONS.

(1) Cold water does not extract from flesh any organic phosphorus compounds which are coagulable by $3\frac{1}{3}$ per cent ammonium sulphate (as it appears to do from blood) and are hydrolyzed to inorganic phosphorus by nitric acid as used in the phosphorus estimation.

(2) In the cold water extracts from 10 to 12 gram samples of flesh, 10 cc. of magnesia-mixture are sufficient for the complete precipitation of all phosphates.

(3) In an extract containing $3\frac{1}{3}$ per cent ammonium sulphate, 48 hours is sufficient time to allow for the complete precipitation of all inorganic phosphates.

REPORT ON NITROGEN.

By R. N. Brackett (Clemson Agricultural College, Clemson College, S. C.), *Referee*, and H. D. Haskins (Agricultural Experiment Station, Amherst, Mass.), *Associate Referee.*

Following the recommendations on nitrogen determination for 1914, the following instructions to collaborators were sent out:

INSTRUCTIONS FOR COLLABORATORS.

Samples are numbered 1 to 6, inclusive.

Samples 1 to 5, inclusive, are to be used for the so-called nitrogen availability determination by the Jones and Street methods.

Samples 1 to 4, inclusive, are raw materials.

Sample 5 is a mixed fertilizer.

Sample 6 is a nitrate to be used for the determination of total nitrogen by the zinc-ferrous sulphate-soda method.

ALKALINE PERMANGANATE METHOD FOR ORGANIC NITROGEN ACTIVITY (JONES[1]).

METHOD I.

With Mixed Fertilizers.

(a) Transfer a sample equivalent to 50 mg. of water insoluble organic nitrogen[2] to an 11 cm. No. 597, S. & S. filter paper and wash with successive portions of water at room temperature until the filtrate measures about 250 cc. When it is found necessary to use 4 or more grams of the original material to secure the 50 mg. of water insoluble nitrogen, *i. e.*, when the percentage of water insoluble nitrogen is 1.25 or less, weigh the required amount into a small beaker, wash by decantation, finally transfer to the filter and finish the extraction as previously directed. When a relatively large amount,

[1] Vt. Agr. Exp. Sta. *Bull.* 173, 238.

[2] Determined by extracting 1 gram of the material on an 11 cm. No. 597, S. & S. filter paper with water at room temperature, until the filtrate measures about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper, if necessary.

i. e., 7–10 grams, of a fertilizer is to be extracted, it is desirable to weigh out duplicate portions. One portion is used for the determination of nitrogen activity by the alkaline permanganate method, and the other is Kjeldahled for its nitrogen content. Compare the latter figure with the result previously obtained from the 1 gram extraction[1] and in case of any marked discrepancy, *i. e.*, over 0.05% of nitrogen, calculate the nitrogen activity on the basis of the exact nitrogen equivalent used.

(b) Transfer the residue from the filter with 20 cc. of water to a 500–600 cc. Kjeldahl distillation flask (round-bottomed preferred, but, if flat-bottomed is used, incline at an angle of 30°). Add 15–20 small glass beads or fragments of pumice stone to prevent bumping, and 100 cc. of alkaline permanganate solution (25 grams of pure potassium permanganate and 150 grams of sodium hydroxid, separately dissolved in water, the solutions cooled, mixed and made to volume of 1 liter). Finally add a piece of paraffin about the size of a small pea to prevent frothing. Connect with an upright condenser to which a receiver containing standard acid has been attached. Digest slowly, below distillation point, with very low flame, using coarse wire gauze and asbestos paper between flask and flame, for at least 30 minutes. Gradually raise the temperature and when danger (if any) from frothing has ceased, distil until 95 cc. of distillate is obtained, and titrate as usual. In cases where a tendency to froth is noticed, lengthen the digestion period and no trouble will be experienced when the distillation is begun. During the digestion, gently rotate the flask occasionally, particularly if the material shows a tendency to adhere to the sides (it is recommended that as nearly as possible 90 minutes be taken for the digestion and distillation). The nitrogen thus obtained is the active water insoluble organic nitrogen.

METHOD II.

With Raw Materials[2].

Transfer a sample equivalent to 50 mg. of water insoluble organic nitrogen[1] to a small mortar, add about 2 grams of powdered rock phosphate[3], mix thoroughly, transfer to a fllter and wash with successive portions of water at room temperature until the filtrate measures about 250 cc. When much oil or fat is present, it is well to wash somewhat with ether before extracting with water. Proceed as directed under (b).

MODIFIED NEUTRAL PERMANGANATE METHOD FOR THE AVAILABILITY OF ORGANIC NITROGEN (STREET[4]).

Weigh a quantity of the fertilizer, equivalent to 50 mg. of water insoluble organic nitrogen[1], on a moistened 11 cm. No. 597, S. & S. filter paper, and wash with successive portions of water at room temperature until the filtrates measure 250 cc. Transfer the insoluble residue with 25 cc. of tepid water to a 300 cc. low-form Griffin beaker, add 1 gram of dry sodium carbonate and 100 cc. of 2% permanganate solution. Digest in a steam or hot water bath for 30 minutes at the temperature of boiling water, cover the beaker with a watch glass and set well down into the bath so that the level of the

---

[1] Determined by extracting 1 gram of the material on an 11 cm. No. 597, S. & S. filter paper with water at room temperature, until the filtrate amounts to about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper, if necessary.

[2] If results are not concordant by Method I (a) and (b), use Method II.

[3] Pass through a sieve with 1 mm. round perforation.

[4] *J. Ind. Eng. Chem.*, 1912, **4**: 437–8.

liquid in the beaker is below that of the bath. Stir twice at intervals of 10 minutes. At the end of the digestion remove from the bath, add 100 cc. of cold water and filter through a heavy 15 or 18½ cm. No. 588, S. & S. folded filter. Wash small quantities at a time with cold water, until total filtrate amounts to about 400 cc. or, if necessary, until on evaporation of about 10 cc. of the runnings no brown residue of oxid of manganese is obtained on ignition. Determine nitrogen in the residue and filter, correcting for the nitrogen of the filter.

(1) Follow these two methods, without variation, exactly as described.

(2) Make all determinations of nitrogen, total, water-insoluble, and permanganate-insoluble as follows:

Place 0.5 gram (in the case of the water-insoluble, and of the permanganate-insoluble nitrogen, the *residue* in which the nitrogen is to be determined) in a digestion flask; add 5 grams of potassium sulphate (powdered), 0.25 gram of crystallized copper sulphate and 25 cc. of sulphuric acid (sp. gr. 1.84). Place the flask over a low flame and heat below the boiling point until the solution is practically colorless, then raise the heat until the solution boils sufficiently to condense and clean the side and neck of flask. Do not keep at a high heat too long. After all adhering particles are washed down by the condensing acid, reduce the heat until the contents of the flask boil gently, and continue the heat until clear and practically colorless. Time should not be over nor much less than 2 hours. Dilute when cold, and proceed with the distillation as in the regular Kjeldahl process, without, of course, the addition of potassium sulphid.

(3) Use at least N/2 acid and alkali for the titration of the ammonia from the permanganate-insoluble residue; that is, not more than half as strong as that used for total or for water-insoluble nitrogen, unless you are already using a N/10 alkali.

(4) Determine the so-called ammoniacal nitrogen by distilling a portion of each sample with magnesium oxid[1].

(5) Report results in per cent as follows:

Street Method.	*Jones Method.*
Total nitrogen.	Total nitrogen.
Ammoniacal nitrogen.	Ammoniacal nitrogen.
Water-insoluble organic nitrogen.	Water-insoluble organic nitrogen.
Permanganate-insoluble nitrogen.	Nitrogen liberated by alkaline permanganate digestion.

TOTAL NITROGEN IN SAMPLE 6.

METHOD I.

To 0.5 gram of the nitrate in a 600–700 cc. flask, add 200 cc. of water, 5 grams of powdered zinc, 1–2 grams of crystallized ferrous sulphate, and 50 cc. of sodium hydroxid solution (36° Baumé). Place some glass wool in the neck of the flask and connect with the distillation apparatus. Distil off the ammonia and collect as usual in N/10 sulphuric acid and titrate.

METHOD II.

Weigh 5 grams, dissolve in water in a 250 cc. flask, pipette 25 cc. and proceed as in Method I.

Determine moisture in all samples in the following manner:

Heat 2 grams in a weighing bottle (1 inch diameter by 2 inches in height) for 5 hours in a water oven at the temperature of boiling water.

[1] *J. Assoc. Official Agr. Chemists*, 1916, **1**: No. 4 (II), 10.

KJELDAHL-GUNNING-ARNOLD METHOD WITH MERCURY AND WITH COPPER SULPHATE.

In order to compare the Kjeldahl-Gunning-Arnold method with the use of mercury and copper sulphate in place of mercury, determine the total nitrogen in Samples 1–5, inclusive, not only as previously described but also as follows:

Place 0.50 gram in a digestion flask, add 5 grams of powdered potassium sulphate, 0.70 gram of mercuric oxid and 25 cc. of sulphuric acid (sp. gr. 1.84). Place the flask over a low flame and heat below the boiling point until the solution is practically colorless, then raise the heat until the solution boils sufficiently to condense and clean the side and neck of the flask. Do not keep at a high heat too long. After all adhering particles are washed down by the condensing acid, reduce the heat until the contents of the flask boil gently, and continue to heat (not over nor much less than 2 hours) until clear and practically colorless. Dilute when cold, add potassium sulphid solution and proceed with distillation as in the regular Kjeldahl process.

The samples selected were as follows:

No. 1, dried blood.
No. 2, 9 parts of tartar pomace and 1 part of dried blood.
No. 3, nitrolene.
No. 4, nitrogenous manure.
No. 5, mixed fertilizer—about 3.30% nitrogen (2% from nitrogenous manure, 1% from dried blood, and 0.30% from tartar pomace).
No. 6, nitrate of soda.

TABLE 1.

Comparative results on samples submitted for cooperative work.

SAMPLE AND ANALYST	MOISTURE	TOTAL NITROGEN		AMMONIA NITROGEN	WATER-INSOLUBLE ORGANIC NITROGEN	JONES METHOD		STREET METHOD	
		GUNNING-ARNOLD METHOD WITH MERCURY	GUNNING-ARNOLD METHOD WITH COPPER			NITROGEN LIBERATED BY ALKALINE PERMANGANATE	ACTIVITY WATER INSOLUBLE ORGANIC NITROGEN	PERMANGANATE INSOLUBLE ORGANIC NITROGEN	ACTIVITY WATER INSOLUBLE ORGANIC NITROGEN
SAMPLE 1 DRIED BLOOD	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	
R. B. Deemer	15.07	12.84	12.48	0.217	12.12	9.16	76	...	..
C. G. Remsburg	....	12.72	12.72	....	....	...	..	...	..
C. F. Inman	14.97	12.78	12.75	0.240	12.23	9.42	77	0.99	92
O. F. Jensen	15.97	12.46	12.27	0.210	12.06	9.26	77	1.20	90
V. B. Hausknecht	11.85	12.88	12.80	0.200	12.56	9.50	76	1.30	90
H. A. Hudgins	12.84	....	12.65	....	12.26	...	..	1.30	89
G. F. Anderson	15.85	12.76	12.42	0.21	12.32	9.24	75	0.78	93
R. D. Caldwell	14.36	12.62	12.59	0.10	12.02	8.61	72	1.16	90
H. D. Spears	15.01	12.76	12.80	0.21	12.08	6.58	54	1.60	87
W. E. Thrun	15.74	12.22	12.62	0.23	11.69	8.31	71	3.38	..
H. S. Chilton	14.07	....	12.38	0.34	11.93	9.44	79	1.37	89
L. W. Bradley	12.35	12.88	12.78	0.22	12.32	7.91	64	0.80	93
R. E. Ingham	15.06	12.93	12.73	0.17	12.20	5.31	44	1.60	87
E. E. Sawyer	14.01	12.58	12.26	0.20	11.92	8.83	74	0.87	93
SAMPLE 2 TARTAR POMACE AND DRIED BLOOD									
R. B. Deemer	10.57	5.58	5.38	0.54	4.68	2.28	49	...	..
C. G. Remsburg	....	5.47	5.44	...	...	...	..	...	..
C. F. Inman	10.38	5.36	5.43	0.49	4.87	1.79	37	1.51	69
O. F. Jensen	12.27	5.19	5.22	0.52	4.69	2.48	53	1.52	67
V. B. Hausknecht	8.20	5.50	5.48	0.53	4.97	2.32	47	1.82	63
H. A. Hudgins	7.62	...	5.44	...	4.84	...	..	0.96	60
G. F. Anderson	11.15	5.34	5.26	0.49	4.77	2.48	52	1.37	71
R. D. Caldwell	11.25	5.38	5.41	0.42	4.91	2.27	46	1.45	70
H. D. Spears	10.30	5.41	5.32	0.49	4.66	1.26	27	0.65	86
W. E. Thrun	11.72	5.29	5.41	0.52	4.51	1.56	35	2.05	54
H. S. Chilton	10.61	...	5.10	0.58	4.66	1.92	41	1.80	61
L. W. Bradley	8.33	5.54	5.50	0.51	5.04	1.93	38	1.26	75
R. E. Ingham	10.41	5.48	5.49	0.42	5.01	1.84	37	1.83	63
E. E. Sawyer	9.79	5.40	5.24	0.50	4.71	2.09	44	1.48	68
SAMPLE 3 NITROLENE									
R. B. Deemer	6.50	7.26	7.02	0.22	2.60	1.09	42	...	..
C. G. Remsburg	...	7.15	7.10	0.21	2.65	...	..	...	..
C. F. Inman	6.30	7.10	7.10	0.24	2.82	0.91	32	0.64	77
O. F. Jensen	7.46	6.91	6.87	0.21	2.49	0.90	36	0.74	70
V. B. Hausknecht	6.15	7.07	7.13	0.21	2.51	0.91	36	0.70	72
H. A. Hudgins	6.86	...	6.78	...	2.84	...	..	0.51	82
G. F. Anderson	7.14	7.02	7.08	0.21	2.63	1.03	39	0.55	79
R. D. Caldwell	8.58	6.94	7.04	0.23	2.29	1.02	44	0.61	73
H. D. Spears	6.75	7.07	7.00	0.17	2.46	1.31	53	0.46	81
W. E. Thrun	7.78	6.86	7.03	0.21	2.44	0.59	24	0.65	73
H. S. Chilton	7.44	...	6.72	0.25	2.60	1.08	41	0.83	68
L. W. Bradley	5.85	7.06	7.02	0.22	2.80	1.40	50	0.49	82
R. E. Ingham	6.68	7.16	7.18	0.19	3.13	0.94	30	0.74	76
E. E. Sawyer	6.85	7.07	6.95	0.20	2.66	1.19	45	0.68	74

TABLE 1.—Continued.

Comparative results on samples submitted for cooperative work.

SAMPLE AND ANALYST	MOISTURE	TOTAL NITROGEN: GUNNING-ARNOLD METHOD WITH MERCURY	TOTAL NITROGEN: GUNNING-ARNOLD METHOD WITH COPPER	AMMONIA NITROGEN	WATER-INSOLUBLE ORGANIC NITROGEN	JONES METHOD: NITROGEN LIBERATED BY ALKALINE PERMANGANATE	JONES METHOD: ACTIVITY WATER INSOLUBLE ORGANIC NITROGEN	STREET METHOD: PERMANGANATE INSOLUBLE ORGANIC NITROGEN	STREET METHOD: ACTIVITY WATER INSOLUBLE ORGANIC NITROGEN
SAMPLE 4 NITROGENOUS MANURE	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	
R. B. Deemer	7.26	8.44	8.17	0.24	6.28	4.10	65	...	..
C. G. Remsburg	...	8.26	8.21	0.23	6.28	...	..	...	..
C. F. Inman	7.56	8.44	8.44	0.21	6.30	3.76	60	0.70	89
O. F. Jensen	9.27	8.09	8.00	0.25	3.31	2.69	81	1.68	49
V. B. Hausknecht	7.78	8.35	8.47	0.22	6.42	4.13	64	0.66	89
H. A. Hudgins	6.86	...	8.30	...	6.18	...	..	0.87	86
G. F. Anderson	9.00	8.28	8.20	0.21	6.42	4.17	65	0.90	86
R. D. Caldwell	9.42	8.16	8.32	0.25	6.56	5.25	80	6.18	91
H. D. Spears	7.98	8.34	8.12	0.23	6.33	3.00	47	1.24	80
W. E. Thrun	8.51	8.02	8.27	0.24	6.22	3.02	48	1.20	80
H. S. Chilton	8.45	...	8.04	0.36	6.31	3.06	48	1.03	83
L. W. Bradley	6.58	8.34	8.28	0.23	6.44	3.90	61	1.10	82
R. E. Ingham	8.03	8.29	8.34	0.20	6.38	3.26	51	1.45	77
E. E. Sawyer	8.18	8.29	8.20	0.24	6.44	3.81	59	0.76	88
SAMPLE 5 MIXED FERTILIZER									
R. B. Deemer	7.14	3.57	3.56	...	...	...	..	...	..
C. G. Remsburg	...	3.43	3.39	0.15	2.56	...	..	...	..
C. F. Inman	7.42	3.48	3.42	0.09	2.77	1.58	57	0.39	86
O. F. Jensen	9.53	3.27	3.38	0.14	2.54	1.59	62	0.41	84
V. B. Hausknecht	4.88	3.36	3.49	0.13	2.74	1.81	66	...	..
H. A. Hudgins	5.59	...	3.21	...	2.68	...	..	0.31	89
G. F. Anderson	8.51	3.44	3.36	0.11	2.70	1.67	62	0.30	89
R. D. Caldwell	9.08	3.32	3.57	0.16	2.59	...	..	...	..
H. D. Spears	7.46	3.41	3.45	0.09	2.47	1.32	52	0.17	93
W. E. Thrun	8.38	3.32	3.39	0.11	2.54	1.20	47	0.52	80
H. S. Chilton	7.56	...	3.22	0.19	2.46	1.39	57	0.41	83
L. W. Bradley	5.55	3.54	3.47	0.12	2.82	1.27	45	0.50	82
R. E. Ingham	...	...	3.45	0.09	2.66	1.14	43	0.70	73
E. E. Sawyer	5.78	3.42	3.44	0.10	2.65	1.53	57	0.34	87

TABLE 2.

Sample 6.—Nitrogen by Zinc-Iron Soda Method.

ANALYST	MOISTURE	0.5 GRAM SAMPLE	5 GRAMS IN 250 CC. USING 25 CC. ALIQUOT
	per cent	*per cent*	*per cent*
R. B. Deemer	0.87	16.51	16.85
C. G. Remsburg	...	15.25	14.95
C. F. Inman	...	15.84	15.86
O. F. Jensen	1.35	15.39	....
V. B. Hausknecht	1.05	16.13	15.91
H. A. Hudgins	....	....	....
G. F. Anderson	1.07	15.50	15.44
R. D. Caldwell	1.40	15.70	15.75
H. D. Spears	1.15	15.23	....
W. E. Thrun	1.53	15.60	15.78
H. S. Chilton	1.81	15.32	....
L. W. Bradley	1.30	15.30	15.28
E. E. Sawyer	0.93	15.90	15.80

DISCUSSION OF RESULTS.

JONES AND STREET METHODS FOR NITROGEN ACTIVITY.

TABLE 1.—SAMPLES 1–5, INCLUSIVE.

In the discussion of these results only the total nitrogen in the column headed "Gunning-Arnold method with copper" will be considered in this connection.

Water-insoluble organic nitrogen.—On the whole, the results are fairly satisfactory. They appear more uniform than those obtained last year on the same samples. Perhaps this is due in part to the use of the Gunning-copper instead of the Gunning-mercury method this year, as it appears from comparative work on total nitrogen that there was less variation with the former than with the latter method.

Nitrogen liberated by alkaline permanganate (Jones method).—The results are very disappointing. Only about 50 per cent show a reasonable agreement, except in the case of Sample 3 where about 70 per cent are fair.

Activity of water-insoluble organic nitrogen (Jones method).—Only about 50 per cent of the results show a reasonable agreement.

Permanganate-insoluble organic nitrogen (Street method).—These results are also rather disappointing. As usual, however, there is less variation than in the Jones method for the liberated nitrogen. The majority of the results on Sample 1 are too high, indicating incomplete washing of the permanganate residue. About one-third of the results on Samples 2

and 4 are also too high. The results are quite satisfactory on Sample 3 and, omitting Spears, highly satisfactory on Sample 5, the complete fertilizer.

Activity of water-insoluble organic nitrogen (Street method).—These results show a much greater uniformity and closer agreement than do the results obtained by the Jones method, as has been the case generally in comparative work on these two methods.

ZINC-FERROUS SULPHATE-SODA METHOD.

TABLE 2.—SAMPLE 6.

In most cases there is little difference in the results whether a 0.5 or 5 gram sample be weighed, made to volume and a 0.5 gram aliquot taken.

In the table the results of Ingham should be rejected, as they were obtained by the modified Gunning method. If the two results over 16 per cent also be rejected and the remainder of the results in the column headed "0.5 gram sample" alone be considered, these nine results fall into three groups: (1) five results, 15.23—15.39, average 15.30; (2) two results 15.50 and 15.60, average 15.55; and (3) two results, 15.70 and 15.84, average 15.77. The first average differs from the second by 0.25 and from the third by 0.47 and the second average from the third by 0.22 per cent. While individual workers, who reported more than one result (and most of them did)obtained very closely agreeing results, the referee does not think the results as a whole warrant the adoption of this method as official without further work. The opinion of the referee is further strengthened by the fact that, whereas more than half of the results fall in the first group (1), R. E. Ingham obtained by the modified Gunning method 15.68 and 15.64, by the official Kjeldahl method[1] 15.60, 15.72 and 15.68, by the official Gunning method[2] 15.82, 15.73 and 15.78, and C. F. Inman obtained 15.70 by both the Kjeldahl-Gunning with oxid of mercury and with copper sulphate, which would indicate that the results reported in groups (2) and (3) are the most correct.

TOTAL NITROGEN.

KJELDAHL-GUNNING-ARNOLD METHOD WITH OXID OF MERCURY AND WITH COPPER SULPHATE.

The results are quite satisfactory with both of these methods, with good agreement, but a slight tendency to higher results with oxid of mercury.

---

[1] *J. Assoc. Official Agr. Chemists*, 1916, **1**: No. 4 (II), 5.
[2] Ibid., 7.

TABLE 3.

Comparative results Kjeldahl-Gunning-Arnold Method with oxid of mercury and with copper sulphate.

METHOD	TOTAL NUMBER OF RESULTS	MAXIMUM DIFFERENCE	GOOD RESULTS			AVERAGE
			NUMBER	MINIMUM	MAXIMUM	
SAMPLE 1 DRIED BLOOD		*per cent*		*per cent*	*per cent*	*per cent*
Kjeldahl-Gunning-Arnold with copper	13	0.53	7	12.65	12.80	12.75
Kjeldahl-Gunning-Arnold with mercury	11	0.71	7	12.72	12.88	12.80
SAMPLE 2 TARTAR POMACE AND DRIED BLOOD						
Kjeldahl-Gunning-Arnold with copper	13	0.40	9	5.38	5.50	5.44
Kjeldahl-Gunning-Arnold with mercury	11	0.39	7	5.38	5.58	5.44
SAMPLE 3 NITROLENE						
Kjeldahl-Gunning-Arnold with copper	13	0.46	10	7.00	7.18	7.07
Kjeldahl-Gunning-Arnold with mercury	11	0.40	8	7.02	7.26	7.11
SAMPLE 4 NITROGENOUS MANURE						
Kjeldahl-Gunning-Arnold with copper	13	0.47	8	8.12	8.32	8.23
Kjeldahl-Gunning-Arnold with mercury	11	0.42	8	8.26	8.44	8.34
SAMPLE 5 MIXED FERTILIZER						
Kjeldahl-Gunning-Arnold with copper	13	0.36	11	3.36	3.57	3.45
Kjeldahl-Gunning-Arnold with mercury	10	0.30	7	3.36	3.57	3.46

CONCLUSIONS.

(1) In the zinc-ferrous sulphate-soda method for nitrates, the results of the different workers are too variable. The chief difficulty in the manipulation of the method lies in the distillation with the use of glass wool in the neck of the flask. Further work should be done on this method without the use of the glass wool, with special reference to the inclination of the flask in the distillation, the use of a flask with a long neck, and the rate of distillation. It may be found, as Mr. B. F. Robertson, of South Carolina, stated last year[1], that though this method has

[1] *J. Assoc. Official Agr. Chemists*, 1915, **1**: No. 3, 390.

the merit of rapidity, it requires too close attention to details where a large number of determinations have to be carried on at the same time. Certainly the method needs and appears to warrant further investigation.

(2) Further work is necessary on the determination of the water-insoluble organic nitrogen. A better agreement this year between the results of the workers in different laboratories is probably due to the use of the Gunning-copper method, but perhaps more to the use by all workers of 1 gram instead of different amounts for the Jones and for the Street method. A preliminary washing in all cases with denatured alcohol, or some similar cheap organic solvent, would likely obviate the difficulty mentioned by some workers in wetting the material, and in preventing agglomeration.

(3) The results of the work on the Jones and Street methods this year confirm the belief in the usefulness of these two methods for distinguishing between good and bad organic ammoniates. More work is necessary on the details of the manipulation to insure uniformity of results. The use of pumice stone to prevent bumping and of paraffin to prevent frothing has been found helpful in this laboratory. As difficulty has been found by many in transferring the residue from the paper to the flask for the alkaline permanganate digestion with only 20 cc. of water, it would be well possibly to use 30–35 cc. of water and distil a proportionally larger amount of distillate. In the case of the Street method, it might be well to increase the strength of the permanganate solution so as to conform to the Jones method, and also to use the amount of water above recommended in transferring the residue from the paper to the beaker for the permanganate digestion. It might be well also to experiment on filter paper in order to find a more rapid filtering paper for the filtration and washing of the permanganate residue, as suggested by W. J. Jones, jr., of Indiana.

(4) The results obtained with the Kjeldahl-Gunning-Arnold method with copper sulphate in lieu of oxid of mercury and with oxid of mercury alone, were very satisfactory, there being a good agreement and practically no difference in the averages. The oxid of mercury seems to be a little more effective and rapid in its catalytic action than copper sulphate and perhaps the digestion in the case of copper should be more prolonged than with mercury, as indicated by the work of Mr. A. J. Patten, of Michigan[1]. Mr. C. G. Remsburg gave some results on time of digestion with Kjeldahl-Gunning-Arnold method, presumably with mercury oxid, using Sample 1, dried blood, and found that the maximum was reached in two hours, though there was an increase of only 0.03 per cent from the result obtained in one hour digestion. It would hardly

[1] *J. Assoc. Official Agr. Chemists*, 1915, **1**: No. 3, 395.

seem necessary to continue any further work on these two modifications of the Kjeldahl-Gunning-Arnold method, especially as they have been adopted as official.

RECOMMENDATIONS.

It is recommended—

(1) That the zinc-ferrous sulphate-iron method for nitrates be further studied, with a view to final adoption as official in 1916.

(2) That the Jones and Street Methods for the determination of organic nitrogen activity be further studied during the coming year, with the special purpose in view of improving or modifying the manipulations in the conduct of each process, so as to increase the accuracy of the water-insoluble organic nitrogen determinations; and, in the case of the Jones method, to overcome the difficulties in the distillation with alkaline permanganate, as well as with the residue for digestion from the paper to the flask; and, in the case of the Street method, to overcome the like difficulty in the transfer of the residue from the paper to the beaker for digestion with permanganate, and also to devise a way of hastening the filtration and washing of the permanganate residue.

(3) That the Kjeldahl-Gunning-Arnold Method with the use of oxid of mercury, or with copper sulphate be adopted as official.

(4) That the use of sodium sulphate in place of potassium sulphate in the Gunning Method and its modifications be studied by the next referee.

SYMPOSIUM ON DETERMINATION OF NITROGEN IN FERTILIZERS.

By P. F. Trowbridge (Agricultural Experiment Station, Agricultural College, N. Dak.).

Answers to a questionnaire on methods of determination of nitrogen in fertilizers were received from 38 station chemists and from 17 commercial chemists.

WEIGHT OF SAMPLE:

21 station and 12 commercial chemists use a 1 gram sample.
8 station and 5 commercial chemists use 0.7 gram or multiple thereof.

DIGESTION WITH SULPHURIC ACID:

41 chemists use mercury (34 metal, 7 oxid).
9 chemists use copper (1 metal, 8 sulphate).
5 chemists use the Gunning method.

Of the 50 chemists using mercury or copper, 33 use in addition potassium sulphate which modification is not official for fertilizers.

Thirty-two chemists do not use potassium permanganate at the close of the digestion. Of the 23 who use potassium permanganate, 12 use potassium sulphate and either mercury or copper, which is not official for fertilizers.

STANDARD ACID:

31 chemists use sulphuric acid, 24 hydrochloric acid.
5 chemists use acid stronger than half-normal.

TITRATION OF THE EXCESS OF ACID:

22 chemists use ammonium hydroxid.
28 chemists use sodium hydroxid.
3 chemists use potassium hydroxid.

INDICATOR:

42 chemists use cochineal. Methyl red, methyl orange, congo red, sodium alizarin sulphonate, alizarin red and lacmoid are also used.

COMPARISON OF AMMONIUM HYDROXID WITH SODIUM HYDROXID.

At the Missouri station laboratory 203 samples of fertilizers were analyzed in duplicate, but at different times. One sample was titrated with ammonium hydroxid and the other with sodium hydroxid.

19 samples gave exact duplication.

79 samples gave higher results with ammonium hydroxid.

105 samples gave higher results with sodium hydroxid.

The average for the 203 samples showed 0.01 per cent higher by the use of sodium hydroxid.

INVESTIGATIONS OF THE KJELDAHL METHOD FOR THE DETERMINATION OF NITROGEN.

By I. K. PHELPS, and H. W. DAUDT[1] (Bureau of Chemistry, Washington, D. C.).

This paper is a preliminary report of an investigation the object of which is to secure, if possible, a modification of the Kjeldahl method applicable to the determination of nitrogen in all organic substances. In this investigation the conditions affording the most efficient digestion and its limitations have been studied.

[1]Present Address, Jackson Laboratory, E. I. Du Pont Co., Wilmington, Del.

For this study special care was taken to obtain the various compounds in the purest condition. For this reason salts of definite composition were often used in place of the compound itself; for example, pyridin zinc chlorid. The ammonium sulphate, with which the processes were checked, was obtained from the products of hydrolysis of pure cyanacetic ester with hydrochloric acid. Ammonium salts obtained from the commercial source are from gas liquors and, hence, contain pyridin substances even after repeated purification.

The distillations were made in the usual manner, except that they were conducted very slowly. Fifth-normal hydrochloric acid and N/10 sodium hydroxid solutions were employed. Sodium alizarin sulphonate was the indicator used.

A very refractory compound, pyridin zinc chlorid, was hydrolyzed with various mixtures commonly used in modifications of the Kjeldahl method. Approximately 0.3 gram of the compound was hydrolyzed for each analysis.

Excellent results were obtained when the digestion was made for $2\frac{1}{2}$ hours with a *boiling* mixture of 25 cc. of sulphuric acid, 0.7 gram of mercuric oxid and 10 grams of potassium sulphate. When the sodium sulphate was substituted for an equal weight of potassium sulphate the results obtained were below the theory, the error equaling as much as 10 per cent of the total nitrogen. In order to investigate the effect of varying proportions of potassium sulphate or of sodium sulphate and sulphuric acid in the presence of mercury, return condensers, constructed entirely of lead, were placed in the neck of the flask during hydrolysis. These served not only to prevent the vaporization of sulphuric acid but also to retain the acid ammonium sulphate even when excessive quantities of potassium sulphate were employed.

It was found that with the lead condensers the relative amounts of potassium sulphate and sulphuric acid in the presence of mercury determine the completeness of the hydrolysis. For instance, when 25 cc. of acid and 10 grams of potassium sulphate were used, incomplete decomposition was obtained, but when 15 cc. of sulphuric acid were used with amounts of potassium sulphate varying from 10 to 30 grams, excellent results were obtained. When more potassium sulphate was employed the results were somewhat lower. These results indicate the cause of the frequent variations observed in duplicate analyses, using the potassium sulphate-sulphuric acid mixture in an open flask. Sodium sulphate seemed to give varying results.

Experiments conducted with potassium sulphate, sulphuric acid, and various metallic catalysts showed that the hydrolysis of pyridin zinc chlorid is complete only when 0.7 gram of mercuric oxid is present. Mercuric oxid present in the proportion of 0.2 gram is insufficient for

complete hydrolysis. Copper sulphate, nickel sulphate, potassium aluminum sulphate, zinc chlorid, manganese chlorid, manganese dioxid, tungstic acid, molybdic acid, titanic acid, or vanadic acid under the conditions caused incomplete hydrolysis. It is to be noted that in the presence of 0.7 gram of mercuric oxid hydrolysis is complete without the presence of copper sulphate.

The hydrolysis of certain organic compounds of various constitutions was studied. In the presence of 0.7 gram of mercuric oxid, 10 grams of potassium sulphate, and 25 cc. of sulphuric acid, weights of the compound varying from 0.2 to 0.4 gram were hydrolyzed completely by $2\frac{1}{2}$ hours boiling. The hydrolysis was found to be complete for the compounds grouped below.

Glucosamin hydrochlorid.
Pyrol derivative:
  Isatin.
Pyrolidin derivatives:
  Atropin.
  Cocain.
Pyridin derivatives:
  Nicotin zinc chlorid.
  Nicotinic acid.
Piperidin derivative:
  B-Eucain hydrochlorid.
Quinolin derivatives:
  Hydroxyquinolin.
  Cinchonidin.
  Strychnin.
  Brucin.
Isoquinolin derivatives:
  Papaverin.
  Narcotin.
  Morphin.
  Hydrastinin.
Purine derivative:
  Caffein.
Imidazole or glyoxalin derivatives:
  Lophin.
  Amarin.
  Histidin dihydrochlorid.
Quinoxalin derivative:
  Quinoxalin hydrochlorid.
Quinazolon derivatives:
  2-Methyl 4-quinazolon.
  2-Methyl 3-phenyl 4-quinazolon.

NOTES ON USE OF POTASSIUM PERMANGANATE IN DETERMINING NITROGEN BY THE KJELDAHL METHOD.

By WILLIAM FREAR, WALTER THOMAS, and H. D. EDMISTON (Agricultural Experiment Station, State College, Pa.).

A marked discrepancy in the results of two experienced analysts on a sample of mixed fertilizer containing nitrates, both using the Scovell modification of the Kjeldahl method with the addition of potassium permanganate, was noted. Scovell[1] at first recommended the use of permanganate in his method but later found that for a certain range of material it was unnecessary. The addition of permanganate was practiced as a precaution in analyzing mixtures of unknown composition. The sole difference in the procedure used by the two analysts was the time when permanganate was added. One of them made the addition

[1] U. S. Bur. Chem. *Bull.* 16, 65.

immediately after the source of heat had been removed, while the other allowed a few moments to elapse.

Kjeldahl[1] questioned the use of permanganate in connection with the ordinary procedure, but found no loss of ammonia from this source under conditions maintained by him. He uses the word *immediately* in describing the time which should elapse between removing the source of heat and the addition of permanganate. The adverb is not sufficiently precise to meet the requirements of the case. It might mean *instantly* or after a short time.

To determine if the exact time of addition of permanganate affected the results, determinations were made by two analysts on several fertilizer samples, with and without nitrates, varying the quantity of permanganate added and the manner and time in relation to completion of the heating process.

Nitrogen determinations with or without permanganate (by Scovell[a] salicylic acid modification unless otherwise noted).

SAMPLE	ANALYST	TIME OF DIGESTION (HOURS)	NITROGEN PERCENTAGES			NOTES REGARDING METHOD
			WITHOUT PERMANGANATE	WITH PERMANGANATE	LOSS WITH PERMANGANATE	
			SERIES I.			
8[b]	Walter Thomas..	2	2.86 2.88	2.12	0.75	In Series I when permanganate was used, 0.8 gram of Baker's nitrogen-free salt was added instantly upon extinguishing the flame under the digestion flasks.
8[b]	H. D. Edmiston..	2	2.79	2.27	0.52	
8[b]	Walter Thomas..	3	2.85	2.28	0.57	
8[b]	H. D. Edmiston..	3	....	2.11	....	
8[b]	Walter Thomas..	4	2.83	....	....	
8[c]	Walter Thomas..	3	2.85	2.36	0.49	
7	Walter Thomas..	2½	2.04	1.21	0.83	
7	H. D. Edmiston..	2½	2.10	1.60 1.51 1.25	0.50 0.59 0.85	
3259	Walter Thomas..	2¾	1.93	1.49	0.44	
3396	Walter Thomas..	2¾	2.99	2.56	0.43	
3407[b]	Walter Thomas..	2¾	1.54	0.94	0.60	

[a] Mercury and sodium hyposulphite used.
[b] Sample contained nitrate.
[c] Determination by plain Kjeldahl process.

[1] *Z. anal. Chem.*, 1883, **22**: 375.

Nitrogen determinations with or without permanganate (by Scovell[a] salicylic acid modification unless otherwise noted).—Continued.

SAMPLE	ANALYST	TIME OF DIGESTION (HOURS)	NITROGEN PERCENTAGES			NOTES REGARDING METHOD
			WITHOUT PERMANGANATE	WITH PERMANGANATE	LOSS WITH PERMANGANATE	
			SERIES II.			
3258[b]	H. D. Edmiston..	2¾	3.65	3.45	0.20	In Series II when permanganate was used, its addition was begun instantly after the flame was extinguished, but was made a very little at a time. The amount added was 0.5 gram, except in the case of the last two trials of Sample 3506, when it was 1.5 and 3.5 grams, respectively.
3271	H. D. Edmiston..	2¾	2.52	2.18	0.34	
3309	H. D. Edmiston..	2¾	2.11	1.81	0.30	
3324	H. D. Edmiston..	2¾	2.04	1.71	0.33	
3506[b]	Walter Thomas..	2¾	2.03	1.83	0.20	
3506[b]	Walter Thomas..	2¾	....	1.39	0.64	
3506[b]	Walter Thomas..	2¾	....	1.48	0.55	
			SERIES III.			
3478	Walter Thomas..	2¾	3.30	3.00 (a) 2.64 (b)	0.30 0.66	In Series III permanganate, amount not recorded, was not added in one case; in a second case (a) gradually; in a third case (b) all at once. A single sample was used, and the addition begun instantly upon extinguishing the flame.
			SERIES IV.			
3259	Walter Thomas..	3	1.91	1.61	0.30	In Series IV, 1 gram of permanganate was added instantly upon extinguishing the flame, to the first two samples, all at once; to the second pair, gradually.
3309	Walter Thomas..	3	2.23	1.91	0.32	
3442	Walter Thomas..	3	4.73	4.60	0.13	
3271	Walter Thomas..	3	2.62	2.32	0.30	

[a] Mercury and sodium hyposulphite used. [b] Sample contained nitrate.

Nitrogen determinations with or without permanganate (by Scovell[a] salicylic acid modification unless otherwise noted).—Continued.

SAMPLE	ANALYST	TIME OF DIGESTION (HOURS)	NITROGEN PERCENTAGES			NOTES REGARDING METHOD
			WITHOUT PERMANGANATE	WITH PERMANGANATE	LOSS WITH PERMANGANATE	
			SERIES V[b].			
3506	Walter Thomas..	2½	2.10	1.78 (a)	0.30	0.7 gram added during 30 seconds, beginning instantly after flame was extinguished.
3506	Walter Thomas..	2½	2.07	1.82 (a)	0.26	
3506	Walter Thomas..	2½	2.06	1.90 (b)	0.18	0.6 gram added as in (a).
3506	Walter Thomas..	2½	2.08	1.99 (c)	0.09	0.3 gram added as in (a).
3506	Walter Thomas..	2½	2.10	2.01 (d)	0.07	0.2 gram added during 30 seconds, but beginning 30 seconds after flame was extinguished.
	Average.....	.....	2.08			
3506	Walter Thomas..	2½	....	1.98 (e)	0.10	0.7 gram added during 30 seconds, but beginning 1 minute after removal of flame.
3506	Walter Thomas..	2½	....	2.05 (f)	0.03	0.2 gram added as in (e).
3506	Walter Thomas..	2½	....	2.12 (g)	....	0.7 gram added during 30 seconds, but beginning 2 minutes after removal of flame.
3506	Walter Thomas..	2½	....	2.08 (g)	....	
3506	Walter Thomas..	2	....	1.82 (h)	0.26	0.7 gram added in 4 seconds at once after removal of flame.
3506	Walter Thomas..	2	....	2.06 (i)	0.02	0.7 gram added in 4 seconds, beginning 1 minute after removal of flame.
3506	Walter Thomas..	2	....	1.78 (j)	0.30	1.0 gram added as in (i).
3506	Walter Thomas..	2	....	1.68 (k)	0.40	1.0 gram added as in (h).
3506	Walter Thomas..	2	....	2.10 (l)	....	0.7 gram added as in (g).
3506	Walter Thomas..	2	....	1.90(m)	0.18	0.7 gram added during 1½ minutes beginning instantly after removal of flame.

[a] Mercury and sodium hyposulphite used.
[b] Determinations of Series V were confined to a single sample.

Nitrogen determinations with or without permanganate (by Scovell[a] salicylic acid modification unless otherwise noted).—Continued.

SAMPLE	ANALYST	TIME OF DIGESTION (HOURS)	NITROGEN PERCENTAGES			NOTES REGARDING METHOD
			WITHOUT PERMANGANATE	WITH PERMANGANATE	LOSS WITH PERMANGANATE	
SERIES V[b].—Continued.						
3506	Walter Thomas..	2	....	1.79 (n)	0.29	0.7 gram added in small quantities *during digestion* when liquid was brown; liquid digested 3 minutes after the addition, until colorless.
3506	Walter Thomas..	2	....	1.68 (o)	0.40	Like (m), but 3 grams added.
3506	Walter Thomas..	2	....	2.06 (p)	0.02	1.0 gram of lead peroxid substituted for permanganate.

[a] Mercury and sodium hyposulphite used.
[b] Determinations of Series V were confined to a single sample.

These results show that for the considerable range of fertilizer mixtures represented the addition of permanganate causes a distinct loss of nitrogen. The loss depends somewhat upon the amount of permanganate, but chiefly upon the time of addition. If the addition is delayed for two minutes after removal from the flame, no loss is observed. This implies that there is a critical temperature below which the reaction causing the loss does not take place.

Four observations of temperature in the digestion flasks about the time of completion of digestion were made. For the plain Kjeldahl method 328°, 329°, 329° and 327°C. were observed. The modified Scovell method gave 344°, 345°, 342° and 345°C. Attempts were made to measure the rate of cooling but were unsuccessful. The fall is quite rapid—approximately 100°C. in two minutes after removal from flame.

Kjeldahl, in the paper above mentioned, states that when permanganate is added the reaction is vigorous enough to cause evolution of light. No case of the appearance of luminosity was noted when permanganate was added at the instant of removal from the flame. This phenomenon occurred chiefly during the period from the fourth to the twelfth minute after removal from the flame. Kjeldahl's mention of the occurrence of luminosity suggests that the time of its addition must have been longer after the removal from the flame than the adverb "immediately" would indicate.

REPORT ON TESTING CHEMICAL REAGENTS.

By C. O. Ewing[1] (Bureau of Chemistry, Washington, D. C.), *Referee.*

The subject of testing chemical reagents has been given some attention by the Bureau of Chemistry and the results have fully justified the effort. Manufacturers know that only the better grades will be accepted and it is rare that lower grades are offered. The few exceptions, however, are sufficient to justify the testing of all chemicals received.

It has been difficult to obtain absolute alcohol which will contain 99.8 per cent or more of absolute alcohol and 10 mils of which will not decolorize 1 drop of 1 : 1,000 potassium permanganate in 10 minutes. This, in the opinion of the referee, is because the manufacturers do not take the heart of the distillate but try to stretch each run as far as possible. The Bureau of Chemistry now makes its own absolute alcohol which contains 99.9 to 99.95 per cent of absolute alcohol.

Methyl alcohol has been rejected because of excessive residue on evaporation, the residue varying from 40 to 70 mg. per 100 cc.

Difficulty has been experienced in obtaining amyl alcohol boiling between 128° and 132°C. Amyl alcohol consists of varying proportions of iso-amyl-alcohol (b. p. 131°C.) and normal amyl alcohol (b. p. 128°C.). When poorly made it may contain lower boiling alcohols. If 90 per cent distils over between 128° and 132°C. it can be considered satisfactory.

An excessive amount of residue was found in absolute ether preserved in cork-stoppered bottles. The stoppers have been protected and no further trouble experienced. One sample of benzol contained an appreciable amount of carbon disulphid. Few samples of animal charcoal complied with the specifications of the Bureau of Chemistry of "Not more than 4 per cent ash, and an extract with 3 per cent potassium hydroxid colored not deeper than light straw". A new type of charcoal used in a number of the Bureau of Chemistry laboratories, known as "Ebonite", has given great satisfaction.

Difficulty was experienced in obtaining satisfactory sodium silicate (40 per cent). Specifications were furnished the manufacturers as follows: "The total sodium oxid to silicon dioxid should be not less than 40 per cent. The proportion of sodium oxid to silicon dioxid should be between the ratio of 1 : 2.4 and 1 : 2.6." A satisfactory product was then obtained.

The following specifications were drawn up for asbestos:

(1) The material should be prepared from pure long-fiber asbestos which has been shredded in such a manner as to leave the fibers loosely separated, varying in length

[1] Present address, United Drug Company, Boston, Mass.

preferably from 1–2½ cm. Fibers should be nearly pure white, with silky luster, capable of fine subdivision when shaken in water, and easily flexed without breaking. The material should possess good matting qualities.

(2) It should be practically free from all impurities and contain not more than traces of iron. (A small fragment of asbestos heated to glowing should show on cooling no perceptible change in color and texture.)

(3) The total loss after heating with 20% hydrochloric acid for 30 minutes and igniting at red heat 30 minutes should not exceed 3%.

Five samples have been received under these specifications. Two complied with the requirements, one losing 3 per cent by the acid-ignition treatment and the other only 1.1 per cent.

One sample of tin-foil was found to contain 97.7 per cent of lead.

The Ninth Revision of the U. S. Pharmacopoeia permits the use of acetanilid as a preservative in hydrogen peroxid. A recent patent mentions the use of cinchonidin. These substances should be guarded against in hydrogen peroxid for use as a reagent.

Potassium hydroxid prepared by electrolysis is easily obtained and is of very good quality for most purposes but may contain up to 0.2 per cent of chlorid. The manufacturers have agreed to change their labels to indicate the presence of chlorid.

A method for determination of alcohol was given which is essentially the same as subsequently published in the Ninth Revision of the U. S. Pharmacopoeia.

RECOMMENDATIONS.

It is recommended—

(1) (a) That chemical reagents labeled "U. S. P." be tested according to the specifications of the U. S. Pharmacopoeia, Ninth Revision (1916).

(b) (Tentative) That, unless otherwise specified, all other chemical reagents be tested according to Merck's "Chemical Reagents, Their Purity and Tests", second edition, 1914, by Henry Schenck. This publication is a standard on the testing of chemical reagents. It represents the work of a great number of chemists, extending over many years. Rather than wait until such a comprehensive set of tests could be worked out by the members of this association, it would seem advisable to adopt this latest revision of Merck.

(2) That the method mentioned above be used for the determination of ethyl alcohol in pharmaceutical preparations.

The methods of this association do not include a general method for alcohol in pharmaceutical preparations. The great diversity of alcoholic pharmaceuticals makes it extremely difficult to provide a method that will apply in every instance. The attempt has been made to prepare a general outline for procedure and then to give the most important and most frequently required modifications. The alcohol refractivity tables

prepared by B. H. St. John have already been presented to the association at a previous session[1].

(3) That the work on methods for the detection and determination of ethyl alcohol, methyl alcohol, amyl alcohol, and acetone be continued, together with work on immiscible organic solvents.

The data at hand appear to warrant a continuation of the study of these chemicals.

On motion of W. W. Skinner, the committee on recommendations of referees and revision of methods was instructed to prepare a form on which referees will be required to submit their several recommendations.

The committee on editing methods of analysis submitted the following report on the definition of the terms "provisional", "optional", and "alternative":

"A 'provisional' method is a method which has been reported by the appropriate committee upon recommendation of referees, published in the proceedings, and approved by the association, but which has not been tested sufficiently to warrant its adoption as an official method.

"The terms 'optional' and 'alternative' have no place in the designation of methods, and in the opinion of your committee should be eliminated."

Approved.

The committee on amendment to the Constitution and By-Laws stated that more time would be necessary before a report could be presented.

Mr. Ross moved that a vote of thanks be given the president, which was unanimously carried.

The convention adjourned, at 4.20 P. M., to meet in Washington, D. C., at the call of the executive committee.

---

[1] *J. Assoc. Official Agr. Chemists*, 1916, **2**: No. 2 (II), 208–35.

PROCEEDINGS OF THE THIRTY-THIRD ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1916.

OFFICERS, REFEREES, ASSOCIATE REFEREES AND COMMITTEES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, FOR THE YEAR ENDING NOVEMBER, 1917.

Honorary President.

H. W. WILEY, Woodward Building, Washington, D. C.

President.

J. K. HAYWOOD, Bureau of Chemistry, Washington, D. C.

Vice-President.

P. F. TROWBRIDGE, Agricultural Experiment Station, Agricultural College, N. Dak.

Secretary-Treasurer.

C. L. ALSBERG, Box 744, 11th Street Station, Washington, D. C.

Additional Members of the Executive Committee.

B. B. Ross, Polytechnic Institute, Auburn, Ala.
H. C. LYTHGOE, State Department of Health, Boston, Mass.

Referees.

Phosphoric acid: W. J. Jones, jr., Agricultural Experiment Station, La Fayette, Ind. (deceased).
Nitrogen: H. D. Haskins, Agricultural Experiment Station, Amherst, Mass.
Potash: T. D. Jarrell, Bureau of Chemistry, Washington, D. C.
Soils: C. B. Lipman, Agricultural Experiment Station, Berkeley, Cal.
Inorganic plant constituents: J. F. Breazeale, Bureau of Plant Industry, Riverside, Cal.
Insecticides and fungicides: O. B. Winter, Agricultural Experiment Station, E. Lansing. Mich.
Water: J. W. Sale, Bureau of Chemistry, Washington, D. C.
Foods and feeding stuffs: (Not appointed.)
Dairy products: J. Hortvet, Old Capitol, St. Paul, Minn.
Saccharine products: M. N. Straughn, Bureau of Chemistry, Washington, D. C. (deceased).

Drugs: W. O. Emery, Bureau of Chemistry, Washington, D. C.
Testing chemical reagents: C. O. Ewing, United Drug Company, Boston, Mass.
Micro-analytical methods: B. J. Howard, Bureau of Chemistry, Washington, D. C.
Food preservatives: A. F. Seeker, U. S. Appraiser's Stores, New York, N. Y. (deceased).
Coloring matters in foods: W. E. Mathewson, Bureau of Chemistry, Washington, D. C.
Metals in foods: David Klein, 1410 Kimball Building, Chicago, Ill.
Fruit and fruit products:
W. D. Bigelow, National Canners Association, Washington, D. C.
M. N. Straughn, Bureau of Chemistry, Washington, D. C. (deceased).
Canned vegetables: W. D. Bigelow, National Canners Association, Washington, D. C.
Cereal foods: J. A. LeClerc, Miner-Hillard Milling Co., Wilkes-Barre, Pa.
Wines: B. G. Hartmann, Transportation Building, Chicago, Ill.
Soft drinks (bottlers' products): W. W. Skinner, Bureau of Chemistry, Washington, D. C.
Distilled liquors: J. I. Palmore, Bureau of Chemistry, Washington, D. C.
Beers: H. S. Paine, Bureau of Chemistry, Washington, D. C.
Vinegars: W. A. Bender, Douglas Packing Co., Rochester, N. Y.
Flavoring extracts: A. E. Paul, Transportation Building, Chicago, Ill.
Meat and meat products: C. E. Marsh, State Department of Health, Boston, Mass.
Edible fats and oils: R. H. Kerr, Bureau of Animal Industry, Washington, D. C.
Spices and other condiments: H. E. Sindall, Austin Nichols & Co., Brooklyn, N. Y.
Cacao products: E. Bloomberg, Pompeian Co., Baltimore, Md.
Coffee: H. A. Lepper, Bureau of Chemistry, Washington, D. C.
Tea: Miss E. A. Read, Bureau of Chemistry, Washington, D. C.
Baking powder: H. E. Patten, Bureau of Chemistry, Washington, D. C.

Associate Referees.

Phosphoric acid:
Basic slag to cooperate with committee on vegetation tests on the availability of phosphoric acid in basic slag: E. C. Shorey, 2706 Harrison Street, Wilmington, Del.
Nitrogen:
Special study of the Kjeldahl method: I. K. Phelps, Bureau of Chemistry, Washington, D. C.
Potash: J. T. Foy, Clemson College, S. C.
Soils:
Nitrogenous compounds: J. K. Plummer, Agricultural Experiment Station, Raleigh, N. C.
Lime requirements: W. H. McIntire, Agricultural Experiment Station, Knoxville, Tenn.
Inorganic plant constituents: (Not appointed.)
Insecticides and fungicides: J. J. T. Graham, Bureau of Chemistry, Washington, D. C.
Water: J. C. Diggs, State Board of Health, Indianapolis, Ind.
Foods and feeding stuffs:
Sugar: A. Hugh Bryan, Arbuckle Bros., Old Slip and Water Streets, New York, N. Y.
Crude fiber: C. K. Francis, Transcontinental Oil Company, Tulsa, Okla.
Stock feed adulteration: Miss B. H. Silberberg, Bureau of Chemistry, Washington, D. C.
Organic and inorganic phosphorus: (Not appointed).
Water: J. O. Clarke, U. S. Custom House, Savannah, Ga.

Dairy products:

Separation of nitrogenous substances in milk and cheese: L. L. Van Slyke, Agricultural Experiment Station, Geneva, N. Y.

Saccharine products:

Maple products: J. F. Snell, Macdonald College, Quebec, Canada.
Honey: S. F. Sherwood, Bureau of Plant Industry, Washington, D. C.
Sugar house products: P. A. Yoder, Bureau of Plant Industry, Washington, D. C.

Drugs:

Medicinal plants: A. Viehoever, Bureau of Chemistry, Washington, D. C.
Alkaloids: H. C. Fuller, Institute of Industrial Research, Washington, D. C.
Synthetic products: C. D. Wright, Bureau of Chemistry, Washington, D. C.
Balsams and gum resins: E. C. Merrill, United Drug Company, Boston, Mass.
Enzyms: V. K. Chesnut, Bureau of Chemistry, Washington, D. C.

Meat and meat products:

Separation of nitrogenous compounds in meat products: P. F. Trowbridge, Agricultural Experiment Station, Agricultural College, N. Dak.
Meat extracts: T. M. Price, Bureau of Animal Industry, Washington, D. C.

Permanent Committees.

Cooperation with Other Committees on Food Definitions.

Wm. Frear (State College, Pa.), *Chairman.*
Julius Hortvet, St. Paul, Minn.
J. P. Street, Indianapolis, Ind.

Recommendations of Referees and Revision of Methods.

(Figures in parentheses refer to year in which appointment expires.)
B. B. Ross (Auburn, Ala.), *Chairman.*

Subcommittee A: A. J. Patten (1918), (Agricultural Experiment Station, E. Lansing, Mich.), *Chairman*, C. C. McDonnell (1922), B. B. Ross (1920). (Phosphoric acid (basic slag to cooperate with committee on vegetation tests on the availability of phosphoric acid in basic slag), nitrogen (special study of the Kjeldahl method), potash, soils (nitrogenous compounds, lime requirements), inorganic plant constituents, insecticides and fungicides and water.)

Subcommittee B: R. E. Stallings, deceased, (1918), (Georgia Department of Agriculture, Atlanta, Ga.), *Chairman*, C. A. Browne (1922), H. C. Lythgoe (1920). (Foods and feeding stuffs (sugar, crude fiber, stock feed adulteration, organic and inorganic phosphorus, water), dairy products (separation of nitrogenous substances in milk and cheese), saccharine products (maple products, honey, sugar house products), drugs (medicinal plants, alkaloids, synthetic products, balsams and gum resins, enzyms), testing chemical reagents and micro-analytical methods.)

Subcommittee C: L. M. Tolman (1918), (Wilson & Company, Chicago, Ill.), *Chairman*, J. P. Street (1922), R. E. Doolittle (1920). (Food preservatives, coloring matters in foods, metals in foods, fruit and fruit products, canned vegetables, cereal foods, wines, soft drinks (bottlers' products), distilled liquors, beers, vinegars, flavoring extracts, meat and meat products (separation of nitrogenous compounds in meat products, meat extracts), edible fats and oils, spices and other condiments, cacao products, coffee, tea, baking powder.)

SPECIAL COMMITTEES.

Board of Editors.

C. L. Alsberg (Bureau of Chemistry, Washington, D. C.), *Chairman.*
E. F. Ladd (1917). R. E. Doolittle (1919).
J. P. Street (1918). L. L. Van Slyke (1920).

Editing Methods of Analysis (U. S. Bur. Chem. Bull. 107, Rev.).

R. E. Doolittle (Transportation Building, Chicago, Ill.), *Chairman.*
W. A. Withers. A. F. Seeker (deceased).
J. P. Street. G. W. Hoover.
B. L. Hartwell.

Vegetation Tests on the Availability of Phosphoric Acid in Basic Slag.

C. B. Williams (College of Agriculture and Mechanic Arts, West Raleigh, N. C.), *Chairman.*
C. G. Hopkins. B. L. Hartwell.
H. D. Haskins. J. A. Bizzell.

Amendment to the Constitution and By-Laws.

B. B. Ross (Polytechnic Institute, Auburn, Ala.), *Chairman.*
C. L. Alsberg. H. D. Haskins.

Committee on Methods of Sampling Fertilizers to Cooperate with a Similar Committee of the American Chemical Society.

C. H. Jones (Agricultural Experiment Station, Burlington, Vt.), *Chairman.*
W. J. Jones, jr. (deceased). B. F. Robertson.

Committee on Revision of Methods of Soil Analysis.

C. B. Lipman (Agricultural Experiment Station, Berkeley, Cal.), *Chairman.*
W. H. McIntire. A. W. Blair.
E. C. Shorey. R. Stewart.

MEMBERS AND VISITORS PRESENT.

Abbott, J. S., Bureau of Chemistry, Washington, D. C.
Ageton, C. N., Central Experiment Station, Santiago de las Vegas, Habana, Cuba.
Albright, A. R., Jackson Laboratory, E. I. Du Pont Co., Wilmington, Del.
Allen, Mrs. Mary S., Bureau of Chemistry, Washington, D. C.
Allen, R. M., Ward Baking Co., New York, N. Y.
Almy, Lloyd H., 1833 Chestnut Street, Philadelphia, Pa.
Alsberg, C. L., Bureau of Chemistry, Washington, D. C.
Appleman, Chas. O., College Park, Md.

Badger, C. H., Bureau of Chemistry, Washington, D. C.
Bailey, H. S., E. I. Du Pont Co., Wilmington, Del.
Bailey, L. H., Bureau of Chemistry, Washington, D. C.
Baker, E. L., Patent Cereals Co., Geneva, N. Y.
Balcom, R. W., Bureau of Chemistry, Washington, D. C.

Barnard, H. E., American Institute of Baking, Minneapolis, Minn.
Bartlett, G. M., Joseph Campbell Co., Camden, N. J.
Bartlett, J. M., Agricultural Experiment Station, Orono, Me.
Baughman, W. F., Bureau of Chemistry, Washington, D. C.
Bell, Chas. E., State Department of Agriculture, Raleigh, N. C.
Bennett, Miss B. M., Bureau of Chemistry, Washington, D. C.
Beyer, G. F., Bureau of Internal Revenue, Washington, D. C.
Bidwell, G. L., Bureau of Chemistry, Washington, D. C.
Bigelow, W. D., National Canners Association, 1739 H Street, N. W., Washington, D. C.
Birckner, Victor, Bureau of Chemistry, Washington, D. C.
Bitting, A. W., National Canners Association, 1739 H Street, N. W., Washington, D. C.
Bizzell, J. A., State College of Agriculture, Ithaca, N. Y.
Blanck, F. C., State Department of Health, 16 W. Saratoga Street, Baltimore, Md.
Blumenthal, P. L., Agricultural Experiment Station, Lexington, Ky.
Borden, N. H., Bureau of Chemistry, Washington, D. C.
Bowling, J. D., jr., State College, College Park, Md.
Boyle, Martin, Bureau of Chemistry, Washington, D. C.
Boyles, F. M., McCormick & Co., Baltimore, Md.
Brackett, R. N., Clemson Agricultural College, Clemson College, S. C.
Bradbury, C. M., State Department of Agriculture, Richmond, Va.
Brattain, P. H., Corby Co., Washington, D. C.
Breckenridge, J. E., American Agricultural Chemical Co., New York, N. Y.
Brewster, J. F., Bureau of Chemistry, Washington, D. C.
Brinton, C. S., Food and Drug Inspection Station, U. S. Appraiser's Stores, Philadelphia, Pa.
Broughton, L. B., College Park, Md.
Brown, B. E., Bureau of Plant Industry, Washington, D. C.
Brown, H. H., Bureau of Chemistry, Washington, D. C.
Bryan, T. J., Calumet Baking Powder Co., Chicago, Ill.
Burnet, W. C., Bureau of Chemistry, Washington, D. C. (deceased).

Campbell, W. G., Bureau of Chemistry, Washington, D. C.
Carpenter, F. B., Virginia-Carolina Chemical Co., Richmond, Va.
Carroll, John S., German Kali Works, Atlanta, Ga.
Cathcart, C. S., Agricultural Experiment Station, New Brunswick, N. J.
Chapin, R. N., Bureau of Animal Industry, Washington, D. C.
Chesnut, V. K., Bureau of Chemistry, Washington, D. C.
Child, Ernest, H. Reeve Angel & Co., 120 Liberty Street, New York, N. Y.
Chittick, J. R., Jaques Mfg. Co., Chicago, Ill.
Clark, A. J., Agricultural College, E. Lansing, Mich.
Clarke, J. O., Food and Drug Inspection Station, U. S. Custom House, Savannah, Ga.
Cochran, C. B., State Dairy and Food Bureau, W. Chester, Pa.
Collins, W. D., Bureau of Chemistry, Washington, D. C.
Conner, S. D., La Fayette, Ind.
Cook, F. C., Bureau of Chemistry, Washington, D. C.
Cross, L. J., Cornell University, Ithaca, N. Y.
Custis, H. H., Bureau of Animal Industry, Washington, D. C.

Darlington, Homer T., Metallurgical Engineer, Natrona, Pa.
Daudt, H. W., Jackson Laboratory, E. I. Du Pont Co., Wilmington, Del.
Davidson, J., Bureau of Chemistry, Washington, D. C.

Davis, R. O. E., Bureau of Soils, Washington, D. C.
Deemer, R. B., Bureau of Plant Industry, Washington, D. C.
Dodge, C. O., Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.
Donk, P. J., National Canners Association, 1739 H Street, N. W., Washington, D. C.
Doolittle, R. E., Food and Drug Inspection Station, Transportation Building, Chicago, Ill.
Doran, J. M., Bureau of Internal Revenue, Washington, D. C.
Doyle, Miss A. M., Room 9114 Du Pont Building, Wilmington, Del.
Dubois, W. L., 215 Galene Street, Milwaukee, Wis.
Dunbar, P. B., Bureau of Chemistry, Washington, D. C.

Eimer, W. R., Eimer & Amend, New York, N. Y.
Eldred, F. H., General Chemical Co., Laurelville, N. Y.
Ellett, W. B., Agricultural Experiment Station, Blacksburg, Va.
Emery, J. A., Bureau of Animal Industry, Washington, D. C.
Emery, W. O., Bureau of Chemistry, Washington, D. C.
Emmons, F. W., Washburn-Crosby Co., Minneapolis, Minn.
Enslow, L. H., Miraflores Filtration Plant, Ancon, Panama, C. Z.
Eoff, J. R., jr., Bureau of Internal Revenue, Washington, D. C.
Eskew, H. L., State Food and Drug Department, Nashville, Tenn.
Ewing, C. O., United Drug Co., Boston, Mass.

Fairchild, J. G., Bureau of Chemistry, Washington, D. C.
Ferris, L. W., Bureau of Chemistry, Washington, D. C.
Fitzgerald, F. F., National Canners Association, 1739 H Street, N. W., Washington, D. C.
Fowler, G. Scott, State Department of Agriculture, Atlanta, Ga.
Fraps, G. S., Agricultural Experiment Station, College Station, Texas.
Frary, G. G., State Food and Drug Commission, Vermilion, S. Dak.
Frear, Wm., State Department of Agriculture, State College, Pa.
French, D. M., Alexandria Fertilizer & Chemical Co., Alexandria, Va.
Frey, R. W., John W. Heald & Co., Lynchburg, Va.
Fry, Wm. H., Bureau of Soils, Washington, D. C.
Fuller, A. V., Bureau of Animal Industry, Washington, D. C.
Fuller, H. C., Institute of Industrial Research, Washington, D. C.
Furber, F. B., Lederle Laboratories, New York, N. Y.

Garby, C. D., Bureau of Chemistry, Washington, D. C.
Gardiner, R. F., Bureau of Soils, Washington, D. C.
Geiger, G. A., 43 Gaston Street, West Orange, N. J.
Gibbs, H. D., E. I. Du Pont Co., Wilmington, Del.
Gillespie, L. J., Bureau of Plant Industry, Washington, D. C.
Goodrich, C. E., Musher & Co., Baltimore, Md.
Gore, H. C., Bureau of Chemistry, Washington, D. C.
Gowen, P. L., Food and Drug Inspection Station, Park Avenue Building, Baltimore, Md.
Grab, Eugene G., National Fruit Product Co., Woodward Building, Washington, D. C.
Graham, J. J. T., Bureau of Chemistry, Washington, D. C.
Grant, D. H., Bureau of Chemistry, Washington, D. C.
Griffin, E. L., Bureau of Chemistry, Washington, D. C.

Hand, W. F., Agricultural and Mechanical College, Agricultural College, Miss.
Harris, H. L., Pacific Coast Borax Co., 100 William Street, New York, N. Y.
Harrison, C. W., Food and Drug Inspection Station, Park Avenue Building, Baltimore, Md.
Hartmann, B. G., Food and Drug Inspection Station, Transportation Building, Chicago, Ill.
Hartwell, B. L., Agricultural Experiment Station, Kingston, R. I.
Hausknecht, V. B., State Department of Agriculture, Harrisburg, Pa.
Haywood, J. K., Insecticide and Fungicide Board, Washington, D. C.
Haywood, W. G., State Department of Agriculture, Raleigh, N. C.
Hazen, Wm., Bureau of Soils, Washington, D. C.
Hellmuth, Everett A., Southern Railroad, Alexandria, Va.
Herff, B. von, McCormick Building, Chicago, Ill.
Hoagland, R., Bureau of Animal Industry, Washington, D. C.
Holland, E. B., Agricultural Experiment Station, Amherst, Mass.
Holman, H. P., Bureau of Chemistry, Washington, D. C.
Holmes, A. D., Jackson Laboratory, E. I. Du Pont Co., Wilmington, Del.
Hoover, G. W., Food and Drug Inspection Station, Transportation Building, Chicago, Ill.
Hortvet, Julius, State Dairy and Food Department, Old Capitol, St. Paul, Minn.
Houghton, H. W., Bureau of Chemistry, Washington, D. C.
Howard, B. J., Bureau of Chemistry, Washington, D. C.
Howes, C. C., Davison Chemical Co., Baltimore, Md.
Hoyt, L. F., Larkin Co., Buffalo, N. Y.
Hubbard, W. S., Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.
Hurst, L. A., Department of Agriculture, Washington, D. C.
Huston, H. A., German Kali Works, 42 Broadway, New York, N. Y.

Irwin, W. H., Swift & Co., Chicago, Ill.

Jacobs, B. R., Bureau of Chemistry, Washington, D. C.
Jacobs, Mrs. B. R., 1502 Meridian Place, N. W., Washington, D. C.
Jarrell, T. D., Bureau of Chemistry, Washington, D. C.
Johns, C. O., Bureau of Chemistry, Washington, D. C.
Jones, C. H., Agricultural Experiment Station, Burlington, Vt.
Jones, D. B., Bureau of Chemistry, Washington, D. C.
Jones, W. J., jr., Agricultural Experiment Station, La Fayette, Ind. (deceased).
Jones, W. P., 3518 Newark Street, Cleveland Park, Washington, D. C.

Keister, J. T., Bureau of Chemistry, Washington, D. C.
Kellogg, J. W., State Department of Agriculture, Harrisburg, Pa.
Kerr, R. H., Bureau of Animal Industry, Washington, D. C.
Klein, David, State Food Department, 1410 Kimball Building, Chicago, Ill.
Klueter, Harry, Dairy and Food Commission, Madison, Wis.
Knight, H. L., States Relations Service, Washington, D. C.
Knight, O. D., Insecticide and Fungicide Board, Washington, D. C.
Kunke, Wm. F., Bureau of Chemistry, Washington, D. C.

LaForge, F. B., Bureau of Chemistry, Washington, D. C.
Lang, H. L., States Relations Service, Washington, D. C.

Lathrop, E. C., Jackson Laboratory, E. I. Du Pont Co., Wilmington, Del.
Law, Thos. C., The Picard Law Co., Atlanta, Ga.
LeClerc, J. A., Miner-Hillard Milling Co., Wilkes-Barre, Pa.
LeCompte, T. R., Department of Agriculture, Washington, D. C.
Lee, R. E., Fleischmann Co., Peekskill, N. Y.
Lepper, H. A., Bureau of Chemistry, Washington, D. C.
Liepsner, F. W., 825 Gravier Street, New Orleans, La.
Linder, W. V., Bureau of Internal Revenue, Washington, D. C.
Lipman, C. B., University of California, Berkeley, Cal.
Lodge, F. S., Armour Fertilizer Works, Chicago, Ill.
Lynch, Wm. D., Bureau of Chemistry, Washington, D. C.
Lythgoe, H. C., State Department of Health, Boston, Mass.

McClelland, Byron, Bureau of Chemistry, Washington, D. C.
McCune, J. S., State Board of Health, Columbus, Ohio.
McDonnel, M. E., Pa. R. R. Co., Altoona, Pa.
McDonnell, C. C., Bureau of Chemistry, Washington, D. C.
McDonnell, H. B., Agricultural Experiment Station, College Park, Md.
McGeorge, W. T., Food and Drug Inspection Station, U. S. Appraiser's Stores, San Francisco, Cal.
McIntire, W. H., Agricultural Experiment Station, Knoxville, Tenn.
Mains, G. H., Massachuesetts Institute of Technology, Cambridge, Mass.
Mallory, G. E., Bureau of Internal Revenue, Washington, D. C.
Mason, G. F., H. J. Heinz Co., Pittsburgh, Pa.
Mastin, M. G., Porto Rico Fruit Exchange, San Juan, P. R.
Mathewson, W. E., Bureau of Chemistry, Washington, D. C.
Merrill, E. C., 77 Gainsborough Street, Boston, Mass.
Middleton, Ellis S., Berwyn, Md.
Miller, C. O., State Department of Health, 16 W. Saratoga Street, Baltimore, Md.
Miller, H. M., National Canners Association, Los Angeles, Cal.
Mitchell, A. S., Bureau of Chemistry, Washington, D. C.
Morgan, W. J., Bureau of Chemistry, Washington, D. C.
Mory, A. V. H., Sears, Roebuck & Co., Chicago, Ill.
Murray, A. G., Bureau of Chemistry, Washington, D. C.

Nealon, E. J., Bureau of Chemistry, Washington, D. C.
Nelson, E. K., Bureau of Chemistry, Washington, D. C.
Nollau, E. H., Experiment Station Record, Department of Agriculture, Washington, D. C.
Nutt, G. S., Bureau of Internal Revenue, Washington, D. C.

Obst, Mrs. Maud Mason, Food Research Laboratory, 1833 Chestnut Street, Philadelphia, Pa.

Paine, H. S., Bureau of Chemistry, Washington, D. C.
Palmer, H. E., Bureau of Chemistry, Washington, D. C.
Palmore, J. I., Bureau of Chemistry, Washington, D. C.
Parkins, J. H., Royster Guano Co., Norfolk, Va.
Parkinson, Miss N. A., Bureau of Chemistry, Washington, D. C.
Patten, H. E., Bureau of Chemistry, Washington, D. C.
Patterson, H. J., Agricultural Experiment Station, College Park, Md.

Phelps, I. K., Bureau of Chemistry, Washington, D. C.
Phelps, Mrs. I. K., 1410 M Street, N. W., Washington, D. C.
Pingree, M. H., American Agricultural Chemical Co., Baltimore, Md.
Plummer, J. K., Agricultural Experiment Station, Raleigh, N. C.
Pope, W. B., Bureau of Soils, Washington, D. C.
Porch, M. B., H. J. Heinz Co., Pittsburgh, Pa.
Power, F. B., Bureau of Chemistry, Washington, D. C.

Rabak, Frank, Bureau of Plant Industry, Washington, D. C.
Rabinowitz, Benjamin, Alart & McGuire Co., Brooklyn, N. Y.
Randall, W. W., State Department of Health, 16 W. Saratoga Street, Baltimore, Md.
Rather, J. B., Standard Oil Company, Chemical Laboratory, Brooklyn, N. Y.
Reed, J. B., Bureau of Chemistry, Washington, D. C.
Remsburg, C. G., State College of Agriculture, College Park, Md.
Roark, R. C., General Chemical Co., Baltimore Md.
Robb, J. B., State Department of Agriculture, Richmond, Va.
Robinson, C. H., Experimental Farm, Ottawa, Canada.
Rodes, Wm., Agricultural Experiment Station, Lexington, Ky.
Rogers, J. S., Kistler-Lesh Co., Morganton, N. C.
Rogers, L. A., Bureau of Animal Industry, Washington, D. C.
Rose, R. E., State Department of Agriculture, Tallahassee, Fla.
Ross, B. B., Polytechnic Institute, Auburn, Ala.
Ross, S. H., Cudahy Packing Co., East Chicago, Ind.
Roth, G. B., Hygienic Laboratory, Washington, D. C.
Rudnick, P., Armour & Co., Chicago, Ill.
Runkel, Homer, Bureau of Chemistry, Washington, D. C.
Runyan, E. G., Hutchins Building, Washington, D. C.

Sale, J. W., Bureau of Chemistry, Washington, D. C.
Sample, J. W., Department of Food and Drugs, Nashville, Tenn.
Samuels, J. A., 133 17th Street, N. W., Washington, D. C.
Savage, Mrs. G. O., 4212 Keokuk Street, N. W., Washington, D. C.
Schreiner, Oswald, Bureau of Plant Industry, Washington, D. C.
Schroeder, J. P., Bureau of Soils, Washington, D. C.
Schwartze, E. W., Bureau of Chemistry, Washington, D. C.
Seeker, A. F., Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y. (deceased).
Seidell, Atherton, Hygienic Laboratory, Washington, D. C.
Sherwood, S. F., Bureau of Plant Industry, Washington, D. C.
Shorey, E. C., 2706 W. Harrison Street, Wilmington, Del.
Shrader, J. H., Bureau of Plant Industry, Washington, D. C.
Sievers, A. F., Bureau of Plant Industry, Washington, D. C.
Silberberg, Miss B. H., Bureau of Chemistry, Washington, D. C.
Simpson, G. E., Yale University, New Haven, Conn.
Sive, Benj. E., Bureau of Standards, Washington, D. C.
Skinner, J. J., Bureau of Plant Industry, Washington, D. C.
Skinner, W. W., Bureau of Chemistry, Washington, D. C.
Smalley, F. N., Southern Cotton Oil Co., Savannah, Ga.
Smith, C. M., Bureau of Chemistry, Washington, D. C.
Smith, H. R., Food and Drug Inspection Station, Park Avenue Building, Baltimore, Md.
Smith, Joseph G., Bureau of Soils, Washington, D. C.

Smither, F. W., Bureau of Standards, Washington, D. C.
Snyder, C. F., Bureau of Standards, Washington, D. C.
Snyder, Harry, Russell Miller Milling Co., Minneapolis, Minn.
Spencer, G. C., Bureau of Soils, Washington, D. C.
Stallings, R. E., State Department of Agriculture, Atlanta, Ga. (deceased).
Steinkoenig, L. A., Bureau of Soils, Washington, D. C.
Stephenson, Chas. H., Bureau of Chemistry, Washington, D. C.
Stewart, Robert, University of Illinois, Champaign, Ill.
Street, J. P., 405 Indiana Trust Building, Indianapolis, Ind.
Sutton, C. G., B. B. Culture Laboratory, 176 Palisade Avenue, Yonkers, N. Y.

Taber, W. C., Food and Drug Inspection Station, Park Avenue Building, Baltimore, Md.
Taistra, Theo., Eimer & Amend, New York, N. Y.
Taylor, A. E., Bureau of Chemistry, Washington, D. C.
Taylor, G. B., Bureau of Animal Industry, Washington, D. C.
Taylor, J. N., Bureau of Animal Industry, Washington, D. C.
Thatcher, R. W., Agricultural Experiment Station, St. Paul, Minn.
Thom, Chas., Bureau of Chemistry, Washington, D. C.
Thomas, C. C., Williams & Wilkins Co., Baltimore, Md.
Thompson, Miss A. R., Bureau of Chemistry, Washington, D. C.
Todd, A. R., Dairy and Food Department, Lansing, Mich.
Toll, J. D., The American Fertilizer, Philadelphia, Pa.
Treuthardt, E. L. P., Purchase and Storage, Subsistence Division, Inspection Branch, Munitions Building, Washington, D. C.
Trowbridge, P. F., Agricultural Experiment Station, Agricultural College, N. Dak.

Valaer, Peter, jr., Bureau of Internal Revenue, Washington, D. C.
Van Slyke, L. L., Agricultural Experiment Station, Geneva, N. Y.
Veitch, F. P., Bureau of Chemistry, Washington, D. C.
Vollertsen, J. J., Morris & Co., Chicago, Ill.
Vrooman, Carl S., Wilmington, Ill.

Waldraff, P. H., General Chemical Co., Hudson Heights, N. J.
Walker, L. S., Agricultural Experiment Station, Amherst, Mass.
Walker, P. H., Bureau of Standards, Washington, D. C.
Walters, E. H., Bureau of Plant Industry, Washington, D. C.
Weatherhead, D. L., Food and Drug Department, Nashville, Tenn.
Weber, F. C., Bureau of Chemistry, Washington, D. C.
Weems, J. B., State Department of Agriculture, Richmond, Va.
Wessling, Miss H. L., States Relations Service, South, Washington, D. C.
White, H. J., State College, College Park, Md.
Wilbert, M. I., Hygienic Laboratory, Washington, D. C.
Wilcox, B. B., Food and Drug Inspection Station, Custom House, Savannah, Ga.
Wiley, H. W., Woodward Building, Washington, D. C.
Wiley, H. W., jr., Woodward Building, Washington, D. C.
Wiley, Samuel W., Wiley & Co., Inc., 7 S. Gay Street, Baltimore, Md.
Wilson, J. B., Bureau of Chemistry, Washington, D. C.
Wilson, S. M., Baugh Chemical Co., Baltimore, Md.
Wise, L. E., Jackson Laboratory, E. I. Du Pont Co., Wilmington, Del.
Withers, W. A., College of Agriculture and Mechanic Arts, Raleigh, N. C.
Woodward, H. E., E. I. Du Pont Co., Wilmington, Del.

PRESIDENT'S ADDRESS[1].

THE PAST, PRESENT AND FUTURE OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

By R. N. BRACKETT (Clemson Agricultural College, Clemson College, S. C.), *President.*

MEMBERS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS:

In casting about for a suitable subject on which to address you, I followed, in all probability, the custom of nearly all past presidents, of reviewing the proceedings of the association, in order to find out the established precedents. I was at first rather surprised to find that my files of the proceedings began with the sixth annual meeting, 1889. Upon reaching the proceedings of the sixteenth annual meeting, I found that our much beloved charter member of this association, its third president, and its secretary for twenty-five years or more, to whom this association owes more than perhaps to any other one man, and who is still identified with us as honorary president, Dr. Harvey W. Wiley, had preserved for us the origin, establishment, and an account of the first fifteen meetings in an "Historical Sketch of the Association of Official Agricultural Chemists"[2]. Dr. Wiley stated that he had prepared this sketch because the earlier reports were not available. The association certainly owes Dr. Wiley a debt of gratitude for having written this sketch, which I commend to all the younger members of this association, together with other interesting historical matter which they will find in the proceedings of the sixteenth annual meeting.

The net result of this review, as far as the addresses of the presidents are concerned, is that with one or two exceptions all of the presidents have made addresses, and with only two or three exceptions the address has been on the work of the association. Had not the only president who really repudiated his address been from South Carolina, I think I would have been strongly tempted to follow his precedent, or rather his lead, since his action never became a precedent, as I am heartily in agreement with President H. J. Patterson, when in his address before this association at its twenty-ninth meeting, 1912, he said[3]: "Each year it becomes more and more difficult, or perhaps I would better say that it seems less and less necessary for the president to perform this duty, owing to the fact that the work of the association has already been so well mapped out and covered and the merits and defects so thoroughly appreciated." I, too, have been impressed with the completeness and

[1] Presented Tuesday, November 21, as special order of business for 11.30 o'clock.
[2] U. S. Div. Chem. *Bull.* 57, 16–49.
[3] U. S. Bur. Chem. *Bull.* 162, 109.

thoroughness with which the various presidents have covered the whole field of the association's work, but also with how well they have cultivated, or I might say, harvested the adjacent territory. For example, President Hopkins at the twenty-third meeting gave his notable address on "The Duty of Chemistry to Agriculture"[1]; at the twenty-fifth meeting, President Harry Snyder spoke on "The Training of the Agricultural Chemist"[2]; at the twenty-seventh meeting, President W. A. Withers addressed us on "The Teaching of Chemistry in American Agricultural Colleges"[3]; President G. S. Fraps, at the thirtieth meeting discussed the advances made in agricultural chemistry[4]. So there you are! What is one to do? It appears that everything has got to such a fine state of division that an appropriate subject would now be "Colloid Chemistry" in its various applications. I only wish I were competent to handle that subject, but I can only recommend it to those who come after me.

After considering the matter from various angles, I have decided to risk the criticism or even the opprobrium of the older members of the association, in order to try at least to stir in the newer and younger members, who now make up the majority of its membership, a greater pride and interest in its past achievements, a more vital and sympathetic interest in its present activities, and a patriotic desire, not only to witness, but to have a share in its future development—The Past, Present, and Future of the Association of Official Agricultural Chemists. I can see from your looks that this seems to you to be a very presumptuous theme. My answer is that it is matter of history that "All *gall* is divided into three parts". It will, of course, be necessary for me, in order not to tax your patience too much, to touch some of the three phases of my subject somewhat lightly.

It has been my privilege to have been an active member of this association for only the past six years, although I attended a few sessions of the seventeenth meeting, 1900. This fact will, therefore, account for the statement I am about to make, that the review I have recently made of the proceedings of the association has been to me both enlightening and profitable, nay more, inspiring. The personnel of the membership, the faithfulness in attendance and the unselfish labors of the members, the large amount and excellence of the work which has been done, these and many other things, some of which I wish to revert to again, have excited in me a greater respect and admiration for and appreciation of the past achievements of this association, a more genuine and sympathetic interest in its present welfare, and a keener and more earnest

[1] Ill. Agr. Exp. Sta. *Bull.* 105 (1906).
[2] U. S. Bur. Chem. *Bull.* 122, 110–4.
[3] Ibid., 137, 91–7.
[4] *J. Assoc. Official Agr. Chemists*, 1915, **1**: No. 1 (I), 158–63.

desire to contribute in every possible way to its future development and enlarged usefulness.

May it not be laid down as a general principle, that a familiarity with the history and development of any subject is in very large measure the real basis of one's vital and sympathetic interest in it, and of the actual pleasure derived from working in its fields, as well as the inspiration for such efforts as one is led to put forth in trying to enlarge its boundaries? So strongly do we believe in this principle that all students at Clemson College who pursue the study of chemistry for three years, are required to study the history of chemistry for at least two terms of the third year. The wide appreciation and recognition of this principle is evidenced in the plan, now quite common, of introducing historical references and cuts of the more prominent scientists in the modern textbooks of chemistry and physics especially.

This, then, is my apology, if any be necessary, for the selection of my subject. To the newer and younger members of the association much that I shall say will be new. To the older members, should they be disposed to think they are being imposed upon, I have a story to tell.

Those of you who are familiar with Dr. Wiley's sketch will recall the following interesting facts with regard to the origin and establishment of the association:

"The condition of agricultural chemical work in the United States in 1880 was a peculiar one. The few chemists who were engaged in agricultural research were acting in complete independence of each other in regard to methods of investigation and of research. Some of them were using the methods employed by German chemists, while others followed the instruction given by the French or English agricultural chemists. There was no unity of interest in the profession nor any common system of work. The condition of analytical work may be truly described as chaotic. The result of such condition is easily imagined. There was no standard of comparison or reference. Buyers and sellers were continually wrangling over analyses, which, made by different men following different methods, did not agree.

"The sellers' chemists uniformly obtained higher results than the buyers', and thus the door to litigation was constantly open.

"Strange as it may seem, the first steps toward correcting this pitiable condition did not come from the Department of Agriculture at Washington, but from the department of agriculture of one of the States. It was through the Hon. J. T. Henderson, commissioner of agriculture of Georgia, and at the instigation of Mr. H. J. Redding, now (1899) director of the Georgia station, that the first step toward uniformity of action among agricultural chemists of the United States was taken."

In response to Mr. Henderson's two calls, issued May 20 and July 1, 1880, the first convention of agricultural commissioners and chemists met in the library hall of the Department of Agriculture at Washington, July 28, 1880, with twenty men present. Naturally this body of men consisted chiefly of the commissioners of agriculture, and of representatives of State boards of agriculture, State chemists, and professors of chemistry in State universities and agricultural colleges, from those States using large amounts of commercial fertilizers. The purpose of this meeting, as stated by Mr. Henderson in his first call for the convention, was to secure "such uniformity of method in determining by chemical analysis the percentage of valuable ingredients in commercial fertilizers as will give more uniform and hence more satisfactory results. This is especially desirable in determining 'reverted' phosphoric acid." Among the men who attended this epoch-making meeting are the names of not a few whose names are household words in agricultural chemistry. I commend the reading of the list, which is given in Dr. Wiley's sketch.

The program outlined for discussion at this meeting included the estimation of soluble "reverted" and insoluble phosphoric acid, nitrogen and potash; and, if time allowed, the method of arriving at commercial valuations and the agricultural and commercial valuation of "reverted" phosphoric acid. The entire question of phosphoric acid was referred to a committee of five—Drs. C. U. Shepard, jr., C. A. Goessmann, G. A. Liebig, E. H. Jenkins, and T. R. Wolf. In like manner the question of the estimation of nitrogen and potash was referred to a committee of five—Drs. W. M. Habirshaw, P. B. Wilson, Arthur T. Neale, C. Elton Buck, and N. A. Pratt. These two committees were then given an opportunity to prepare their reports, which were adopted and referred to a committee of two, who should copy them, giving the necessary details of the methods proposed, and send a copy to each member of the convention.

Since so many agricultural chemists were present, it was suggested that it would be well to effect a permanent organization to meet from time to time and discuss topics of interest to the profession, and accordingly the following resolution offered by Dr. C. A. Goessmann was adopted: "Resolved, that this convention form a section in the subdivision of chemistry in the American Association for the Advancement of Science, and that their next meeting be held in Boston during the regular meeting of the aforesaid association."

The second convention of agricultural chemists was held at Boston, August 27, 1880. At this meeting, as the result of a statement of Dr. F. W. Clarke, that there had been inaugurated a movement to have a section of chemistry in the American Association for the Advancement

of Science, the following resolution was adopted: "Resolved, that a committee of three be appointed by the chair (Dr. Goessmann) to take such steps as may be necessary for securing the formation of a permanent chemical section in the American Association for the Advancement of Science, and the establishment of a subsection of agricultural chemistry in such permanent section, should it be formed." The reports of the committees on the estimation of phosphoric acid, nitrogen and potash were made and the methods recommended adopted for one year. The following important resolution was also adopted: "Resolved, that a committee of five be appointed by the chair to secure the cooperation and experimental research of agricultural chemists, to collect and examine the various published methods of fertilizer analysis, and to make a report at the next meeting of this convention; and that we individually pledge ourselves to conduct, for this committee, any experiments or tests which they may desire." Messrs. S. W. Johnson, C. U. Shepard, jr., Peter Collier, W. O. Atwater, and G. C. Caldwell were appointed on this committee. About twenty-five were present at this meeting, which adjourned to meet at the same time and place with the American Association in 1881, the chairman and secretary to hold over.

The third convention of agricultural chemists was held at Cincinnati, August 18, 1881. The outstanding results of this meeting were that no complaints had been heard with regard to the analysis of fertilizers, except as to insoluble or "reverted" phosphoric acid; that the committee of five last mentioned had no report; that some progress was being made toward the formation of a permanent section of chemistry in the American Association for the Advancement of Science; that a long and warm discussion was indulged in on the methods of estimating insoluble or "reverted" phosphoric acid, the commercial chemists favoring the ammonium oxalate and the agricultural chemists the ammonium citrate method. The discussion ended in the appointment of a committee of seven to consider the best method, and its details, for determining insoluble or "reverted" phosphoric acid by the use of ammonium oxalate—one member to be chosen by the chair, three by the president of the Chemical and Fertilizer Exchange, and three to be the State chemists in charge of fertilizer control present at the meeting, viz., Drs. C. W. Dabney, jr., N. W. Lord, and H. C. White. A committee of five was also appointed to continue the investigation of the whole subject of the determination of insoluble or "reverted" phosphoric acid. The chair appointed on this committee Messrs. A. R. Ledoux, C. A. Goessmann, E. H. Jenkins, G. A. Liebig, and C. M. Stillwell. I have given this matter in some detail because this appears to have been the subject upon which this convention split, and we must admit, I think, that the method of determining insoluble phosphoric acid is still a "rock

of offence". Embodied in the published minutes of this meeting are the report of the committee of seven, and also a letter from Dr. S. W. Johnson on the citrate method. A large number of chemists were present at this meeting, and a partial list is given by Dr. Wiley in his sketch. The meeting adjourned to reconvene at the call of the chair, provided a meeting were necessary before their organization as a subsection of the American Association for the Advancement of Science.

In the words of Dr. Wiley, "After the adjournment of the Cincinnati meeting the interest in the collaboration of the agricultural chemists seemed to die out. There was a certain feeling of antipathy—perhaps it is not well to make it so strong as this, but a strong feeling of incongruity existed—between the trade chemists on the one hand and the official chemists on the other. It was an unvoiced sentiment pervading the organization to the effect that an association composed of trade chemists and official chemists contained elements of instability which would prevent it from ever becoming highly useful." Nevertheless, after the lapse of three years, Mr. Henderson again called a meeting of the agricultural chemists which was held in the Senate Chamber of the Capitol at Atlanta, Ga., May 15, 1884. There were present at this meeting, which was the precursor of the organization meeting here today: Judge J. T. Henderson, Prof. H. W. Wiley, Prof. N. W. Lord, Dr. Charles W. Dabney, jr., Prof. William A. Noyes, Dr. Charles U. Shepard, jr., Dr. J. W. Gascoyne, Dr. Allard Memminger, Mr. Philip E. Chazal, Dr. E. H. Jenkins, Prof. S. W. Johnson, Prof. H. C. White, Dr. N. P. Pratt, Mr. G. W. Benson, Mr. N. A. Pratt, Prof. John A. Myers, Prof. J. A. Burns, Mr. L. H. Jones, jr., Mr. C. L. Allen, Mr. G. W. Davison, Prof. W. C. Stubbs, Dr. Arthur T. Neale, Mr. P. T. Pendleton, Mr. C. B. F. Lowe, Mr. Leroy Broun, jr., Mr. C. M. Strahan, Mr. A. F. Crowell, Mr. C. V. Petraeus, Mr. Theo. Schumann, Mr. P. J. Schumann. After the opening address by Judge Henderson, Dr. C. U. Shepard, jr., made an introductory address in which he said, "Again we are assembled to consider the inconsistencies of agricultural chemical analysis. That they pinch all of us there is no doubt." Dr. Shepard insisted that the chemists having official connection with agricultural colleges and experiment stations and boards of agriculture should take the initiative in establishing uniform methods of procedure. As a commercial chemist he expressed his entire willingness to collaborate with the official chemists in every possible way, and also to receive and examine samples which might be submitted for comparative analysis. At this meeting three committees were appointed to consider methods of analysis, as follows:

"(1) On methods of determining phosphoric acid, consisting of Drs. S. W. Johnson, H. C. White, and W. C. Stubbs.

"(2) On methods of determining nitrogen, consisting of Messrs. P. E. Chazal, A. T. Neale, and J. A. Myers.

"(3) On methods of determining potash, consisting of E. H. Jenkins, W. J. Gascoyne, and H. W. Wiley.

"Papers were read by F. B. Dancy, on comparison of some methods of determining 'reverted' phosphoric acid; by Professor Johnson, on comparison of the action of ammonium citrate solution on phosphates at different temperatures; by Dr. Shepard, on certain apparatus for the determination of reduced phosphoric acid; by Dr. Wiley, on the action of ammonium citrate on ground bone, and the Gooch crucible in phosphate estimations; by Dr. Shepard, on the insufficiency of the 'Washington' method when applied to acid phosphates which have lain long in pile; by Dr. Memminger, on determining 'reverted' phosphates by the use of ammonium oxalate; by Dr. Dabney, on the Ruffle and copper oxid methods of determining nitrogen; by C. B. F. Lowe, on the determination of nitrogen from nitrates by the soda-lime process; by Dr. Memminger, on methods of determining potash.

"The reports of the three committees on methods of analysis were received, discussed, amended, and adopted. The bulletin of the proceedings of the Atlanta convention practically forms the first in the series of bulletins containing the methods of analysis of the Association of Official Agricultural Chemists. It was compiled on the plan which was followed for many years thereafter, of having the proceedings and methods contained in the same bulletin, which plan was only abandoned when the volume of matter to be considered was so great as to necessitate two separate publications.

"The convention, when it adjourned, agreed to meet in connection with the American Association for the Advancement of Science, in Philadelphia, the following September.

"The Philadelphia meeting was held September 8, 1884. Dr. E. H. Jenkins was appointed chairman and Dr. C. W. Dabney acted as secretary. A committee appointed at the Atlanta meeting to consider the advisability of organizing the association as a subsection of the American Association for the Advancement of Science, recommended the formation of two associations.

"First. The Association of Agricultural Chemists to be entirely distinct from the American Association to which should be left the discussion of the methods of analysis, etc.

"Second. The subsection of the American Association for the Advancement of Science, to be open to all agricultural chemists for the purposes of investigation and discussion.

"The unanimous opinion expressed in the discussion of this subject was that an organization entirely separate from the American Associa-

tion would best advance the objects of the convention. A committee, consisting of Messrs. H. C. White, E. H. Jenkins, P. E. Chazal, J. A. Myers, and H. W. Wiley, was appointed to consider the form of organization and instructed to report the following day."

"On September 9 a formal organization took place, the present name of the association was adopted, officers for the following year were elected, and the convention resolved into the first annual meeting of the Association of Official Agricultural Chemists. Committees on phosphoric acid, potash, and nitrogen were appointed, and methods for the determination of phosphoric acid and potash in commercial fertilizers adopted as the official methods of the association.

"The bulletin containing the proceedings of this meeting consists of eight pages of printed matter, in which are given the list of officers elected, the constitution, and the methods of analysis adopted officially by the association."

The second annual meeting of the Association of Official Agricultural Chemists was held in the library of the Department of Agriculture, beginning September 1, 1885. The officers of this convention were: President, S. W. Johnson; vice-president, H. C. White; secretary-treasurer, C. W. Dabney, jr.; executive committee, E. H. Jenkins and H. W. Wiley. In the absence of President Johnson, Vice-President White took the chair, and, Dr. Dabney also being absent, Mr. Chazal acted as secretary. Hon. Norman J. Colman, Commissioner of Agriculture, addressed the members, dwelling on the objects of the association, declaring his hearty sympathy with them, and expressing the hope that the association would not limit its attention to uniform methods of fertilizer analysis, but would extend its work to general chemical analysis, and commended to its special attention the standard of purity of foods and methods of detecting adulteration. Reports from the various committees appointed at the previous meeting were received, and several papers on subjects pertaining to the work of the association read. Officers elected for the ensuing year were: President, H. W. Wiley; vice-president, C. W. Dabney, jr.; secretary-treasurer, Clifford Richardson; executive committee, W. J. Gascoyne and H. A. Huston.

By invitation of Commissioner Norman J. Colman the third annual meeting of the association was held at the Department of Agriculture, August 26 and 27, 1886, and through his courtesy the proceedings were published as Bulletin No. 12 of the Division of Chemistry. At the opening of the convention Dr. Wiley, the president, addressed the association, reviewing the work accomplished, presenting in detail the methods of fertilizer analysis in use in foreign countries and comparing them with the methods adopted by the association. Dr. Wiley closed his address by recommending that the investigations of the association

be extended over a wider range of subjects, and expressing the opinion that every problem connected with chemical agricultural analysis was a proper subject for discussion at meetings. He suggested the advisability of appointing a committee to consider the propriety of revising the clause in the constitution which limited the membership and the scope of investigations. Then followed reports on phosphoric acid, potash, and nitrogen, together with various papers on each of the three subjects. For the first time methods were adopted as official for nitrogen determinations, it being decided that the association would recognize as official either the Ruffle, Kjeldahl, absolute or soda-lime methods, when carried out according to the working details to be supplied by the committee. These methods were therefore printed as official methods of the association. Officers elected for the following year were: President, E. H. Jenkins; vice-president, P. E. Chazal; secretary-treasurer, Clifford Richardson; executive committee, H. W. Wiley and M. A. Scovell. At this meeting two additional committees were appointed, namely, on food stuffs and dairy products, and proper methods adopted for the work of each.

The fourth annual convention of the association was held in Washington, August 16, 17, and 18, 1887, in the library of the Department of Agriculture, with thirty-five members present and President Jenkins in the chair. In his address Dr. Jenkins urged particularly an amendment of the constitution so as to admit as members of the association chemists from agricultural colleges who exercised no official control over the analysis of fertilizers, soils, cattle foods, dairy products, and other materials connected with agricultural industry, and also the chemists from the Treasury Department. This amendment was adopted toward the close of the meeting. Then followed in their regular order the report of the committee on the analysis of cattle food, the report on dairy products, phosphoric acid, potash, and nitrogen. In addition to the five existing committees on analytical methods, two more were added at this meeting, namely, one on the analysis of fermented liquors and the other on methods of analysis of sugars.

The fifth annual convention of the association was held in the library of the Department of Agriculture at Washington, August 9, 1888, with President Chazal in the chair. The other officers of this meeting were: vice-president, W. J. Gascoyne; secretary, Clifford Richardson; additional members of the executive committee, John A. Myers and E. H. Jenkins. There occur in the minutes of this meeting three entries worthy of special note: First, that the president omitted the usual address in order to proceed with the business of the convention; second, that Prof. F. W. Clarke, of the Geological Survey, addressed the members of the association on the desirability of forming a national chemical

society, and in harmony with this idea a committee, consisting of Messrs. H. W. Wiley, W. C. Stubbs, and E. A. de Schweinitz, was appointed to represent the association in any action which might be taken in this direction; third, that instead of a committee of three, as was the previous custom, it was decided by the association to put one person, called a Reporter, in charge of each of the subjects considered by the association.

The sixth annual convention of the association was held in the Seed Division of the Department of Agriculture, beginning September 10, 1889, with President John A. Myers in the chair. The other officers of the meeting were: Vice-president, M. A. Scovell; secretary, Clifford Richardson; executive committee, H. W. Wiley and William Frear. The session was opened with an address by Hon. Edwin Willets, Assistant Secretary of Agriculture. President Myers followed with an address of some length, on the objects of the association, laying special stress on the necessity of such accuracy and reliability of methods as to compel respect for and trust in the conclusions of the association, citing statistics showing the influence of the association on commercial activity, and comparing its work with that of foreign nations having the same object in view. The feasibility of organizing a national chemical society was discussed at length and on motion the association approved the proposition. Reports were received from the various committees and disposed of as seemed best. Mr. Richardson resigned the position of secretary and Dr. H. W. Wiley was chosen to fill the vacancy. Thirty-seven members and visitors were present.

The seventh annual convention of the association was held at Washington in the lecture hall of the National Museum, beginning August 28, 1890, with President M. A. Scovell in the chair. The other officers of the meeting were: Vice-president, G. C. Caldwell; secretary, H. W. Wiley; additional members of the executive committee, J. A. Myers and E. H. Jenkins. In his presidential address, Dr. Scovell devoted his time mainly to recommendations in regard to special lines of work of the association. The work on cattle foods had now become so extended that, at this convention, it was deemed necessary to divide the work between two reporters, one to consider foods high in carbohydrates, and the other to devote himself to foods low in carbohydrates. A reporter was also appointed to consider the subject of ash analysis. At the suggestion of the committee on organization of a national chemical society, after conference with a similar committee of the American Association for the Advancement of Science, appointed by Section C, a committee of five from this association was appointed, consisting of Messrs. H. W. Wiley, W. C. Stubbs, G. C. Caldwell, Wm. Frear, and H. H. Nicholson, to cooperate with a similar committee of Section C of the American Association for the Advancement of Science, the Washington Chemical

Society, and similar bodies, in calling a conference of chemists at some central point during the winter to consider the best means of organizing such a society. A committee on ways and means for securing a more thorough chemical analysis of foods and feeding stuffs, and also on a chemical exhibit at the World's Columbian Exposition was appointed at this meeting. Fifty-two members and visitors were present.

We have now given in some detail an account of the circumstances which gave rise to the establishment of this association, and have followed its development for the first seven years of its existence. Someone has said that the first seven years of a child's life are the most impressionable, and that the impressions received during this period of its life persist to maturity and even to old age. This association was most fortunate, and rapidly grew strong and vigorous under the tutelage of such men as S. W. Johnson, G. C. Caldwell, N. T. Lupton, R. C. Kedzie, E. B. Vorhees, W. O. Atwater, M. A. Scovell, and John A. Myers, to mention only a few of those leaders in chemical work and thought who have "passed over the river", and not to speak of those who have been active members of the association almost from the beginning. Nor should we neglect to mention the fostering care of the various Secretaries and Assistant Secretaries of the Department of Agriculture. No wonder the baby grew rapidly! Perhaps I might also compare this association to a great invention. Like all really great inventions, its mother was Necessity, and the inventor, as so often happens, had a very hard time and spent several years trying to find good, substantial, enthusiastic and capable promoters.

With the exception of six meetings (the first at Philadelphia, 1884; tenth at Chicago, 1893; sixteenth at San Francisco, 1899; twenty-first at St. Louis, 1904; twenty-fourth at Jamestown, 1907; and the twenty-sixth at Denver, 1909,) all of the conventions of the association have been held at Washington. For many reasons, which may occur to all of you, the habit of meeting at Washington has contributed in no small measure to the effectiveness of the work which the association has accomplished. It is noteworthy that at least one of the meetings held away from "home", namely, the twenty-first, appears from the proceedings to have been very well attended and to have been in all respects an excellent meeting. (It is also worthy of mention, perhaps, that this meeting was not marred, nor adorned by any presidential address, President Jaffa not having been present.)

Beginning with an average attendance, members and visitors, of less than forty, there were registered as in attendance at the last meeting, the thirty-second, three hundred and twelve, the largest number to date. The average attendance for the ten-year period, seventh to the sixteenth meetings, inclusive, was sixty-four, with a minimum of fifty-two

and a maximum of seventy-seven; and it should be stated that two of these meetings were held away from Washington. The average attendance for the next ten-year period, seventeenth to the twenty-sixth meetings, inclusive, was one hundred and twenty-two, with a minimum of seventy-four (Denver meeting) and a maximum of two hundred and seventeen; and it should be recalled that the St. Louis and Jamestown meetings also occurred in this period, each with an attendance of eighty-eight. For the six-year period, twenty-seventh to thirty-second meetings, inclusive, the average registration has been two hundred and fifty-six, with a minimum of one hundred and eighty-four and a maximum of three hundred and twelve. It would be interesting to plot the curve of attendance. For the past three years there has been a steady increase. May we not hope that this increased attendance and correspondingly growing interest in the work of the association will continue? Those who come to the meetings evidently get something worth while, and my experience for the past six years is that not a few of them also give much. Though more than one of my predecessors in this office has no doubt spoken of the incalculable benefits of such gatherings as these, where we have an opportunity, not only to unburden our souls, talk over our difficulties, and help each other in the solution of the numerous problems which confront us and often become oppressive, but get a chance to learn to know and esteem each other in a friendly way, I cannot refrain from alluding to them again here. Coming as we do from all parts of this great country we should not only, but do, become better Americans as well as better chemists and closer friends. I have no doubt that the annual meetings of this association, by affording opportunities for friendly as well as professional intercourse, have done much to eradicate any delusions or foolish prejudices we of one part of the country may have harbored with regard to another, and have thus helped to weld the North, East, South, and West into one common country.

Beginning with three committees of three on the three subjects, phosphoric acid, nitrogen, and potash, there were added at the third meeting two more committees on food stuffs and dairy products, and again at the fourth meeting two more committees on fermented liquors and sugar. At the fifth meeting these seven committees were replaced by reporters. By a division at the seventh meeting of the subject of cattle foods, an eighth reporter was added. At the eleventh meeting a reporter on tannin, the ninth, was appointed, and for the first time associate reporters are mentioned, their duties not being defined, except to fit themselves for reporters. At the fourteenth meeting (1897) the name "reporter" was superseded by "referee." At the seventeenth meeting the subjects of liquors and foods were divided so as to necessitate the appointment of about fifteen new associate referees, at the sugges-

tion of Dr. A. L. Winton. As you all know, the scope of the work has continued to grow steadily, until now we have seventeen referees and forty-one associate referees, handling about sixteen different subjects with their sub-divisions. This surely does not mean that we have yet covered the whole field of the subjects which this association may legitimately cultivate, nor even that we are doing all that needs to be done in connection with the lines of work we are now pursuing. The recent work undertaken by Dr. I. K. Phelps on the study of the Kjeldahl method suggests the possibility, if not, indeed, the necessity, of the study of many other processes which are ill understood.

As the revision of our methods of analysis is to come up tomorrow for discussion and final adoption in the form of a report of the committee on editing methods of analysis of the association, and since this is probably the most vital matter to be considered at this meeting, it seems proper and timely to say a few words on this subject. As is well known to many of you, the methods of analysis were, up to the twelfth meeting, published as a part of the proceedings, when they were, largely on account of the increased volume of the proceedings, ordered to be printed separately, and appeared in 1895 as Bulletin 46, Division of Chemistry, U. S. Department of Agriculture. Bulletin 46, Revised, was issued in 1899. The Provisional Methods of Food Analysis were printed as Bulletin 65, Division of Chemistry, in 1903. The methods of the association, complete, were first published as Bulletin 107, Division of Chemistry in 1907, and the revised edition in 1908, and finally a reprint issued in 1912. It has now, therefore, been eight years since our methods, as a whole, have been printed in revised form. I am sure that we and all other chemists in the country are looking forward with great satisfaction to the issue of a complete revision to date. It is without possibility of question that the attendance on the meeting when our committee makes its final report should be as large and representative as we can make it. There should be full, but brief and clear-cut, discussion, coupled with constructive criticism of our committee's report.

In discussing the citrate and oxalate methods for "reverted" phosphoric acid at the third meeting of agricultural chemists at Cincinnati in 1881, Professor N. W. Lord said he considered that a great part of the discrepancies and variations was due, not so much to the solvent, but to the differences in carrying out the details. He hoped that whatever method was adopted, the details would be so clearly and plainly stated it would be impossible to have any more trouble on this account.

Mr. N. T. Lupton, in his presidential address at the ninth meeting of this association, 1892, says:

"First, a word in reference to conformity to our prescribed methods. All agree that these should be strictly adhered to in our published

results. As public analysts, our certificates are taken in evidence by the courts of the country, and their money value is of very great importance to manufacturers and others, to say nothing of their higher value as reliable expressions of the composition of the great variety of substances submitted to us for analysis. If these methods are unsatisfactory to any member of the association, the amplest opportunity is given in our annual meetings for the presentation of objections and the adoption of changes, should such be desirable in the opinion of this body. Until such changes are officially made, it is the duty of each and every analyst to conform strictly to the instructions given in our bulletins. Should it, for good and sufficient reasons, be deemed advisable to deviate from official methods, let the results be so stated in unequivocal language. Those who have had much experience in such matters know the disposition of young chemists to make short cuts, and, in a spirit of perfect honesty, to make slight changes here and there in the methods prescribed for their guidance.

"A close examination of the published work of the association will show, I think, a gratifying approximation to uniformity in results, and yet there are perplexing discrepancies not easily accounted for, otherwise than on the ground of deviation from the directions given or want of care in the work."

These quotations would seem to indicate definitely one phase of the discussion of our committee's work. I may add further: Would it, or would it not, be the part of wisdom, and tend to greater uniformity of results, to limit the number of methods designated as official to one (of course giving two as official where we have both a good volumetric and a good gravimetric method), and that one admitted by the majority to be the best and most reliable and workable in the hands of the inexperienced, but skilled and careful analyst, the other methods being understood as for use only as checks? Would it, or would it not, be conducive to uniformity of results to allow less latitude in the use of different reagents in some of our best methods, for example the Kjeldahl for nitrogen? The serious and careful consideration of our committee's report certainly deserves our sanest and best thought.

The respect for and pride in the work of this association which I hope to arouse in the younger members, the increased appreciation of the value and far reaching results of the work it has done and is doing, and the inspiration to give the best they can offer of their talents to its future development and enlarged usefulness, would fall short of my desires should I fail to mention some of the more important movements in which this association has had a share and has often been the determining factor. Among these movements were the formation of a national chemical society—the American Chemical Society; the establishment of

food and drug standards; the passage of the food and drugs act; the adoption of uniform volumetric standards; the passage of the bill establishing the Bureau of Standards; the adoption of uniform methods for fertilizer control, and for reporting analytical results; investigation of methods for testing chemical reagents; the adoption of methods for sampling fertilizers, etc.

What of the future? Is there nothing left to be done? Shall we now "Wrap the drapery of our couches about us and lie down to pleasant dreams"? At the sixth meeting of this association, Mr. John A. Myers, in his presidential address, said, "We strive, first, to secure accuracy; second, rapidity and adaptability of methods of analysis; and, thirdly, uniformity in stating results." It seems to me there is much left to do along all three of these lines. In addition, some of our methods are more expensive than they need be. We need a new method for potash, with platinum at its present price. Sodium compounds for potassium would seem to be called for with potash selling for such prices as now prevail. The following suggestion from Dr. Wm. Frear, in his presidential address at the fourteenth meeting, is well worthy of restatement and careful consideration: "Primarily, the work of the association has been chiefly along the lines of importance to the official chemist. This must still be, to a large extent, true of the association's work. But it will fail of its high opportunities and choose an ideal lower than it may properly select if its work be not pushed also, in a large measure, along more distinctly scientific lines." This should now have even a greater appeal than formerly, since we have our own Journal.

Dr. L. L. Van Slyke, in his presidential address at the eighteenth meeting, gave some suggestions and recommendations, which are as appropriate at this time as when they were made: "Some of our methods of analysis must remain unimproved, unless individual members of the association devote much time to special research." The field is still open and the opportunities numerous. Again, "I believe," he says, "that the time is near at hand when the association should make some effort to encourage and provide for the presentation and discussion at our meetings of papers pertaining to lines of investigations, largely chemical, but not relating necessarily to methods of analysis." Has not this time now actually arrived? This field has certainly not been overworked yet. In reference to expediting the proceedings of the association, there are one or two of Dr. Van Slyke's suggestions which we would do well to follow:

"What we want presented on the floor of our convention are sharp, clear, comprehensive statements of results, with only such detailed explanations as are needed to make those statements readily understood."

Again, "If time may not be saved, interest at least will be increased

if referees and all speakers will develop enough lung power to let others know what they are saying.

"One other suggestion in connection with saving time is the matter of promptness in attendance at the opening of every session."

I wish heartily to endorse all of these suggestions made by Dr. Van Slyke.

In closing these remarks as president, I should fall short of my duty, as painful as it is, did I not announce to you thus officially the passing of three of our active members since we met last in regular annual session as an association:

Professor Robert James Davidson, of the Virginia Polytechnic Institute, Blacksburg, Va., "closed his earthly career suddenly, December 19, 1915, leaving a beautiful and beneficent memory"[1]. After attendance upon the eighth meeting, 1891, Professor Davidson became an active member of the association, and rarely missed a meeting. He served as president at the twentieth meeting, and was otherwise prominent in the work of the association.

Dr. George Edward Patrick, chief, dairy laboratory, Bureau of Chemistry, Washington, D. C., who for many years took an active part in the work of this association, passed to his reward March 22, 1916.

Mr. Thomas Cuthbert Trescot, of the Bureau of Chemistry, Washington, D. C., whose name appears as a member of the association at its third annual meeting, attended its meetings regularly, and took an active and interested part in collaborative work on nitrogen. After a lingering illness, Mr. Trescot was relieved of all suffering April 21, 1916.

All three of these men, our friends and coworkers, were in attendance upon the last meeting of the association. They were faithful to the end, and have received the "Well done, good and faithful servant". I am sure that you will rise and do honor to them as I call their names again: Robert James Davidson, George Edward Patrick, Thomas Cuthbert Trescot.

---

[1] F. K. Cameron. *Science*, 1916, **43**: 418.

FIRST DAY.

MONDAY—MORNING SESSION.

The thirty-third annual convention of the Association of Official Agricultural Chemists was called to order by the President, R. N. Brackett, Clemson College, S. C., on the morning of November 20, 1916, at 10.00 o'clock, at the New Willard, Washington, D. C.

REPORT ON DAIRY PRODUCTS[1].

By Harry Klueter (Dairy and Food Commission, Madison, Wis.), *Referee.*

Owing to the late appointment of the referee, only preliminary work was conducted along the following lines:

(1) The refraction of the sour serum of milk, studying particularly the effect, if any, of pasteurization upon the serum.

(2) Whether or not natural souring would go on in all cases in a pasteurized milk, especially if the milk was not produced under the most sanitary conditions.

(3) Study of pasteurized milks to which viscogen (sucrate of lime) had been added.

RECOMMENDATION.

It is recommended that the above studies be continued.

REPORT ON FOODS AND FEEDING STUFFS.

By A. C. Summers (Department of Agriculture, Commerce and Industries, Columbia, S. C.), *Referee.*

The referee made no report except to recommend that the work be continued for another year with special attention to methods for the determination of crude fiber and crude fat.

J. B. Rather[2] (Agricultural Experiment Station, Fayetteville, Ark.) presented a paper on "The Inosite-Phosphoric Acids of Cottonseed Meal"[3].

---

[1] Presented by P. F. Trowbridge.
[2] Present address, Standard Oil Company, Chemical Laboratory, Brooklyn, N. Y.
[3] Ark. Agr. Exp. Sta. *Bull.* 131, 1–20; *J. Am. Chem. Soc.*, 1917, **39**: 777–89.

Victor Birckner (Bureau of Chemistry, Washington, D. C.) presented papers on "The Acidimetric Titration of Grain Extracts and Amino Acids in the Presence of Alcohol"[1] and "A Simple Method for Measuring the Acidity of Cereal Products. Its Application to Sulphured and Unsulphured Oats"[2].

REPORT ON FEED ADULTERATION[3].

By CARLETON CUTLER[4] (Agricultural Experiment Station, W. La Fayette, Ind.), *Associate Referee.*

The recommendation of last year "That the size of sample of scratch and poultry feeds necessary to get concordant results on quantitative grit determination be further investigated" is the basis of the work reported.

The results given in the following table were secured on samples subsampled by careful quartering, the alternate quarters being discarded until a sample approximating the desired weight was obtained, namely, approximately 10, 25, 50 and 125 grams. Five representative scratch feed samples were chosen and determinations of grit made.

Determination of grit in scratch feeds.

SAMPLE	10[a] GRAMS	25[a] GRAMS	50[a] GRAMS	125[a] GRAMS
	per cent	*per cent*	*per cent*	*per cent*
1	6.0	5.0	3.7	3.4
2	11.9	8.5	5.0	4.9
3	4.0	3.5	3.4	3.3
4	7.4	6.0	5.5	5.0
5	7.5	5.7	5.0	5.0
Average	7.4	5.7	4.5	4.3

[a] Approximately.

Samples of 10 and 25 grams, respectively, gave results from 0.6 to 6.9 per cent, and from 0.1 to 3.5 per cent, higher than where 50 grams were used, with respective averages of 2.9 and 1.2 per cent higher. On the 125 gram basis the results were only from 0.1 to 0.5 per cent lower than on the 50 gram samples, averaging 0.2 per cent lower.

The work of last year showed that 10 grams of feed was too small an amount to secure concordant results in scratch feeds. This year's

[1] *J. Biol. Chem.*, 1919, **38**: 245–54.
[2] *J. Agr. Research*, 1919, **18**: 33–49.
[3] Presented by R. B. Deemer.
[4] Present address, R. F. D. No. 1, Springfield, Vt.

work further confirms this and indicates that not less than 50 grams should be used; increasing the quantity to 125 grams apparently does not increase the accuracy of the determination.

RECOMMENDATIONS.

It is recommended—

(1) That cooperative samples be sent out during the coming year for the determination of grit and weed seeds in scratch feeds.

(2) That a key or outline for the qualitative detection of adulterants in feeding stuffs be prepared and submitted at the next meeting of the association.

REPORT ON CRUDE FIBER[1].

By C. K. FRANCIS[2] (Agricultural Experiment Station, Stillwater, Okla.), *Associate Referee.*

The following instructions were sent to collaborators:

INSTRUCTIONS TO COLLABORATORS.

Material. Two alundum crucibles, two pieces of linen, two samples.

DETERMINATION OF CRUDE FIBER.

Method I.—Official[3].

Make the first filtration through the linen furnished and the second through asbestos. Specific directions for drying and incinerating are given under Method II.

Method II.

(One filtration through alundum crucibles.)

Add to the fat-free residue in an 800 cc. lipless beaker 200 cc. of boiling 1.25% sulphuric acid and boil for 30 minutes, using as condensers round-bottomed flasks filled with cold water or any other form of reflux condenser. A gentle blast of air may be used to overcome foaming. At the end of 30 minutes add 200 cc. of boiling 3.52% sodium hydroxid and continue the boiling for another 30 minutes. Filter rapidly through an alundum crucible by the aid of suction. Much time is saved if the clear liquid is decanted after settling for about 5 minutes. Do not permit the solution to become cold. Wash with boiling water, then with a 1.25% solution of hydrochloric acid (14 cc. of hydrochloric acid made up to 500 cc.), until the washings are acid and then wash free from chlorids with hot water. Dry the crucible and contents at 105°–110°C. and weigh. Burn the material until a white or light gray ash is obtained, cool and weigh. The loss in weight is considered to be crude fiber.

---

[1] Presented by P. F. Trowbridge.

[2] Present address, Transcontinental Oil Co., Benedum-Trees Building, Pittsburgh, Pa.

[3] *J. Assoc. Official Agr. Chemists*, 1916, **2**: No. 2 (I), 118.

Results of collaborative work on crude fiber determinations.

ANALYST	SAMPLE NO. 1 (COTTONSEED MEAL)		SAMPLE NO. 2 (STANDARD WHEAT SHORTS)	
	METHOD I (OFFICIAL)	METHOD II (PROPOSED)	METHOD I (OFFICIAL)	METHOD II (PROPOSED)
	per cent	*per cent*	*per cent*	*per cent*
F. T. Anderson and L. D. Elliott, Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	10.39	Unable to filter	4.79	5.20
Average	10.39	.....	4.79	5.20
F. C. Atkinson, American Hominy Company, Indianapolis, Ind.	10.58	11.25	4.59	4.50
	10.55	11.54	4.54	4.38
Average	10.56	11.40	4.56	4.44
E. H. Berry, U. S. Food and Drug Inspection Station, 1625 Transportation Building, Chicago, Ill.	10.60	12.03	4.63	5.08
	10.55	12.48	4.58	4.95
Average	10.57	12.25	4.60	5.01
F. C. Collier, Inland Revenue Department, Ottawa, Canada.	12.20	12.59	4.92	4.80
Average	12.20*	12.59*	4.92	4.80
F. L. Elliott, Food and Drug Inspection Station, U. S. Custom House, New Orleans, La.	11.78	13.34	5.30	6.65
	11.70	13.32	5.20	6.49
	11.81	13.08	5.19	6.22
	12.22	12.86	5.40	6.55
Average	11.88*	13.15*	5.27*	6.48*
J. W. Enochs, Agricultural and Mechanical College, College Station, Texas.	9.79	.....	4.16	....
	9.92	12.41	4.54	5.24
	9.83	.....	4.66	5.44
Average	9.84	12.41	4.45	5.34
D. T. Evans, jr., Fort Worth Laboratories, Fort Worth, Texas.	10.43	11.77	4.69	5.17
	10.24	12.35	4.66	5.00
	10.49	.....	4.72	....
Average	10.39	12.06	4.69	5.08
Cornelia Kennedy, University of Minnesota, St. Paul, Minn.	10.16	12.48	4.60	5.83
	10.50	12.18	4.59	5.55
Average	10.33	12.33	4.60	5.69
H. G. Lewis, Agricultural College, Agricultural College, Miss.	10.46	.....	4.43	....
	10.27	.....	4.56	....
	10.57	11.75	4.63	4.78
	10.42	.....	4.48	....
	10.27	11.35	4.57	4.71
Average	10.40	11.55	4.53	4.74

Results of collaborative work on crude fiber determinations.—Continued.

ANALYST	SAMPLE NO. 1 (COTTONSEED MEAL)		SAMPLE NO. 2 (STANDARD WHEAT SHORTS)	
	METHOD I (OFFICIAL)	METHOD II (PROPOSED)	METHOD I (OFFICIAL)	METHOD II (PROPOSED)
	per cent	*per cent*	*per cent*	*per cent*
D. G. Morgan, Agricultural Experiment Station, Stillwater, Okla.	10.37 10.25	11.85 11.87	4.61 4.62	4.78 4.80
Average	10.31	11.86	4.61	4.79
J. M. Pickel, Agricultural Experiment Station, Raleigh, N. C.	9.41	11.75	4.21	5.65 5.47
Average	9.41	11.75	4.21	5.56
J. B. Reed, Bureau of Chemistry, Washington, D. C.	11.65	12.30	4.80	5.55
Average	11.65	12.30	4.80	5.55
C. G. Remsburg, College of Agriculture, College Park, Md.	9.32 9.25	9.92 10.32	4.18 4.20 4.18	4.64 4.55 ....
Average	9.29*	10.12	4.19	4.60
W. D. Richardson, Swift & Company, Chicago, Ill. A	10.73 10.75 10.80	11.85 11.85 11.77	4.85 4.90	4.93 4.88 ....
Average	10.76	11.82	4.87	4.90
W. D. Richardson, Swift & Company, Chicago, Ill. B	10.51 10.61 10.47	11.25 11.11 11.22	5.03 4.93	4.98 5.15 ....
Average	10.53	11.19	4.98	5.06
J. H. Roop, Agricultural Experiment Station, La Fayette, Ind.	9.78 9.68	11.82 11.40	4.52 4.33	4.65 4.62
Average	9.73	11.61	4.43	4.63
J. W. Sample, Department of Agriculture, Nashville, Tenn.	9.05 9.03 9.00	11.57 11.47 11.32	.... 4.83 4.87	.... 4.96 4.88
Average	9.03*	11.45	4.85	4.92
R. A. Thuma, University of Minnesota, St. Paul, Minn.	10.55 10.53	12.43 12.61	4.54 4.55	5.68 5.50
Average	10.54	12.52	4.55	5.59
W. E. Thrun, University of Missouri, Columbia, Mo.	10.50 10.56	11.42 11.42	4.73 4.68	4.80 5.06
Average	10.53	11.42	4.71	4.93

Results of collaborative work on crude fiber determinations.—Continued.

ANALYST	SAMPLE NO. 1 (COTTONSEED MEAL)		SAMPLE NO. 2 (STANDARD WHEAT SHORTS)	
	METHOD I (OFFICIAL)	METHOD II (PROPOSED)	METHOD I (OFFICIAL)	METHOD II (PROPOSED)
	per cent	*per cent*	*per cent*	*per cent*
G. P. Walton, Bureau of Chemistry, Washington, D. C.	11.03	11.59	4.93	5.18
	11.11	12.27	4.81	5.52
Average	11.07	11.93	4.87	5.35
W. E. Weber, Department of Agriculture, Harrisburg, Pa.	10.22	11.12	4.81	5.30
	10.32	11.76	4.76	5.18
Average	10.27	11.44	4.78	5.24
C. A. Wells, Experiment Station, Experiment, Ga.	11.25	12.00	4.80	4.66
	11.42	11.94	4.88	4.75
Average	11.33	11.97	4.84	4.70
Average of individual determinations	10.48	11.86	4.64	5.17
Average excluding determinations starred	10.46	11.75	4.58	5.04

COMMENT BY COLLABORATORS.

E. H. Berry: Method I apparently gives more concordant results. It is impossible to say whether the erratic results with Method II are due to the method of boiling or to the use of the alundum crucible.

F. L. Elliott: Considerable difficulty was experienced in filtering through the alundum crucible, especially with Sample 1. With Sample 2 the filtration by this method was fairly satisfactory.

L. D. Elliott: So much difficulty was experienced with the filtration with Method II that the results are unreliable.

J. W. Enochs: Much trouble was experienced in filtering with Method II, especially in the case of the cottonseed meal; in several tests with the latter the liquid could not be filtered at all.

J. W. Kellogg: Method II was followed very carefully, using distilled water. With Method I the second filtration was made through linen filters instead of asbestos. In both methods an electric muffle was used for the incineration.

In Method I a 35 cc. porcelain Gooch crucible was used. The filtration through the alundum crucibles was very unsatisfactory because of the time required.

H. G. Lewis: No difficulty was experienced in filtering through the alundum crucible.

J. M. Pickel: Because of the slowness of filtration and the consequent imperfect washing, the determination by Method II is without value, except as indicating the difficulties of the method when applied to cottonseed meal.

F. B. Porter, Fort Worth Laboratories: I agree with Mr. Evans' statement that the alundum crucible is impractical because of the long time required for filtration.

G. G. Remsburg: No difficulty in filtering was experienced with Sample 2 in either method.

Sample 1 filtered with little difficulty by the official method when care was exercised that the crucible did not filter free of solution at any time. With the one filtration method this sample filtered with difficulty after one-half the solution had passed through. Frequent washing with 1.25% hydrochloric acid was necessary to complete the filtration.

J. H. Roop: Erlenmeyer flasks (800 cc.), fitted with reflux condensers, were used instead of beakers. Method II was more rapid than Method I and gave higher results. In Sample 1 only 83.50% would pass through a 1 mm. sieve. This sample was insufficiently ground to permit concordant results on duplicates, although care was taken to secure as uniform a sample as possible.

J. W. Sample: In the first attempts with Method II, great difficulty was experienced in filtering but later by allowing the solution to stand for 10 minutes more rapid filtration was secured, the filtration and washing being completed in 1 hour. The solutions were not allowed to cool to any great extent before filtering. In each case the first washing was made with 250 cc. of dilute hydrochloric acid, made according to the directions. The material was then washed thoroughly with hot water, dried at 105° for 6 hours, weighed and heated for 1 hour, and weighed again. On material of this character the new method seems to give much higher results than the official method, and as the filtration is so much slower the new method is not considered good.

R. W. Thatcher: Both of our analysts secured higher results by Method II than by Method I, which is undoubtedly due to the methods of digestion rather than to the filtration, as one of our analysts by reversing the methods of filtration obtained results which checked those obtained by following the methods outlined.

W. E. Thrun: Filtering through alundum crucibles is very slow unless the particles are allowed to settle for at least 5 minutes; after washing with the hydrochloric acid solution filtration takes place more rapidly. Linen was used for both filtrations in Method I. It is thought that the mechanical condition of the cottonseed meal may account for the wide results.

G. P. Walton: There was little apparent difference in the speed of filtration between the first and last times these crucibles were used. A solution containing 1.25 grams of sulphuric acid per 100 cc. is not a 1.25% solution, nor is a solution containing 3.52 grams of sodium hydroxid per 100 cc. a 3.52% solution. It is apparent, therefore, that if the theory of the neutralization method is to be made conformable to the official method, using 1.25% solution, a weaker solution than 3.52% sodium hydroxid must be used, viz., one with a normality coefficient of 0.8896, corresponding to an approximately 3.42% solution. No reason is apparent for using a 1.25% hydrochloric acid solution for the final washing out of those substances soluble in hot 1.25% sulphuric acid solution. A solution of hydrochloric acid with a normality coefficient of 0.2566, corresponding in acidity to a 1.25% sulphuric acid solution, would contain approximately 0.93% of hydrochloric acid.

RECOMMENDATIONS.

It is recommended—

(1) That the one filtration method be further investigated.

(2) That the subject of a uniform filtering medium be further studied.

REPORT ON SUGAR[1].

By C. A. Browne (New York Sugar Trade Laboratory, New York, N. Y.), *Referee.*

Experiments were continued upon the modification of the Clerget method whereby 50 cc. of the solution are inverted in a 50 to 55 cc. flask with 5 cc. of concentrated hydrochloric acid and the volume completed to 55 cc. after inversion. The results indicate the accuracy of this modification and a cooperative test should be made by the next referee.

The referee made a detailed study of methods for determining small quantities of reducing sugars in the presence of large amounts of sucrose. Under this condition sucrose undergoes a slight hydrolysis or decomposition, producing substances which reduce the alkaline copper reagent. The amount of this hydrolysis depends on the amount of reducing sugar present. Existing methods for this determination (Meissl, Hiller, Munson and Walker, and others) generally require a preliminary assay in order to determine the concentration necessary for the final determination. The referee is attempting to work out a method that will hold for all concentrations.

It has been shown by the referee[2] that the amount of copper reduced by sucrose was directly proportional to the weight of sucrose and inversely proportional to the weight of reducing sugar in the solution taken for analysis. This reducing action was found for cane molasses, sirup, and similar products not to be expressed exactly by the quantity $\frac{S}{G}$ but by the modification $\frac{S}{G+a}$ in which S represents the milligrams of sucrose by Clerget, G the uncorrected milligrams of glucose corresponding to the weight of reduced copper, and a an analytical constant which is unchanged for any given method. If Allihn's method is used the value of a is 40.

Curves plotted for a wide range of values using the formula $\frac{S}{G+40}$ begin to deviate from actual results obtained by analysis when the sucrose approaches very large amounts and reducing sugars very small amounts. Concentrations of sucrose up to 9 grams in 25 cc. show an increase in reducing action; between 9 and 15 grams the reducing action is approximately constant; and with amounts exceeding 15 grams in 25 cc. the action undergoes a decrease. This decrease may be due to the formation of complex sucrates of copper and potassium, whose coefficient of dissociation decreases as the sucrose content increases as suggested by Maquenne[3], but in the referee's opinion it is due to the

[1] Presented by W. D. Horne.
[2] *J. Am. Chem. Soc.*, 1906, **28**: 450.
[3] *Compt. rend.*, 1915, **161**: 617–23.

excess of sucrose holding a part of the reduced cuprous oxid in a state of colloidal suspension.

While it is impossible to establish any simple numerical relationships between the reducing power of sucrose and invert sugar for all concentrations, the referee has found it possible to do this algebraically for as high concentrations as are necessary in ordinary analysis.

If it is desired to correct for the retarding influence of high concentrations of sucrose upon the reduction when using Allihn's method, the formula $\frac{S}{G+40}$ is modified to $\frac{S}{G+40+\frac{S\,3^2}{1000\,G^2}}$. The quantity $\frac{3\,S^2}{1000\,G^2}$ is negligible

TABLE 1.

Correction for the reducing action of sucrose on Allihn's copper solution.

TAKEN		GLUCOSE FOUND (G)	CORRECTION (C) $\frac{S}{G+40+\frac{3\,S^2}{1000\,G^2}}$	CORRECTED GLUCOSE (G—C)	ERROR
SUCROSE (S)	GLUCOSE				
mgs.	*mgs.*	*mgs.*	*mgs.*	*mgs.*	*mgs.*
250	50.0	52.3	2.7	49.6	— 0.4
250	100.0	102.8	1.8	101.0	+ 1.0
250	150.0	151.8	1.3	150.5	+ 0.5
250	200.0	199.0	1.0	198.0	— 2.0
500	100.0	104.5	3.2	101.3	+ 1.3
500	150.0	153.2	2.6	150.6	+ 0.6
500	200.0	203.2	2.0	201.2	+ 1.2
500	250.0	251.3	1.6	249.7	— 0.3
1000	50.0	60.3	9.9	50.4	+ 0.4
1000	100.0	108.2	6.7	101.5	+ 1.5
1000	200.0	205.3	4.1	201.2	+ 1.2
1000	250.0	252.0	3.4	248.6	— 1.4
2000	50.0	66.6	18.3	48.3	— 1.7
2000	100.0	113.7	12.9	100.8	+ 0.8
2000	200.0	207.5	8.1	199.4	— 0.6
2000	250.0	255.5	6.7	248.8	— 1.2
3000	00.0	26.5	28.6	— 2.1	— 2.1
3000	50.5	75.8	24.9	50.9	+ 0.4
3000	202.2	212.8	11.8	201.0	— 1.2
5938	62.5	101.0	39.2	61.8	— 0.7
5625	49.9	91.6	41.6	50.0	+ 0.1
5938	25.6	70.3	45.0	25.3	— 0.3
6000	00.0	41.7	41.8	— 0.1	— 0.1
6125	11.2	58.2	46.5	11.7	+ 0.5
6125	25.0	69.7	46.8	22.9	— 2.1
9000	00.0	50.2	48.2	2.0	+ 2.0
12000	00.0	49.0	44.6	4.4	+ 4.4
15000	00.0	50.9	42.7	8.2	+ 8.2

for amounts of sucrose less than 1 gram, but with quantities much above 1 gram retardation in its reducing power becomes so pronounced that a correction must be made.

The application of this formula to the analysis of known mixtures of sucrose and dextrose is given in Table 1.

The referee has investigated a method of determining reduced copper[1] by igniting the crucible containing the cuprous oxid and then plunging the hot crucible into vapors of methyl alcohol. Reduction to metallic copper is almost instantaneous. A similar method using ethyl alcohol has been proposed by Wedderburn[2]. The alcohol used for reduction should be changed frequently since oxidation products may interfere with complete reduction to metallic copper. There is also danger of decomposition of alcohol and deposition of carbon if the crucible is too hot or the alcohol too strong. The method is not one which can be depended upon in the hands of unskilled chemists. Its simplicity renders it serviceable and it is recommended to the next referee for further study.

RECOMMENDATIONS.

It is recommended—

(1) That the modifications proposed last year for determining sucrose by acid and invertase inversion be further studied.

(2) That the work upon determining small amounts of reducing sugars in the presence of sucrose be continued.

(3) That the methods of determining copper by reduction of the oxid in alcohol vapors be investigated.

(4) That the optical methods for estimating raffinose in beet products be examined with special reference to hydrolysis by means of enzyms.

RECOMMENDATIONS ON SUGAR.

By W. D. Horne (National Sugar Refining Company, Yonkers, N. Y.).

It is recommended—

(1) That the referee on sugar investigate the mixing of raw sugar samples in a mortar instead of on a plate, to diminish moisture changes.

(2) That the referee on sugar investigate the defecation with the minimum amount of lead subacetate requisite to cause flocculation, and to avoid an excessive quantity for producing a lighter colored filtrate than is necessary to obtain a reliable reading.

---

[1] *Z. Zuckerind. Bohmen*, 1897-8, **22**: 216–21.
[2] *J. Ind. Eng. Chem.*, 1915, **7**: 610–1.

(3) That polarizations be checked by readings above and below, rather than by averaging.

(4) That polarizations be made at 20°C. or that temperature correction for levulose be included with that for sucrose.

(5) That the Bureau of Standards be asked to certify to the most advisable Baumé scale, and that it be adopted.

WATER IN FOODS AND FEEDING STUFFS.

By W. J. McGee (Bureau of Chemistry, Food and Drug Inspection Station, San Juan, P. R.), *Associate Referee.*

The referee found it impossible to undertake any work upon this subject. For future work, it is recommended that a study be made of the best method of determining the moisture in each kind of food or feeding stuff. The determination of moisture in cottonseed meal has been under consideration by the Cottonseed Crushers' Association for some time. It might be profitable to make a study of that.

Even though it may take a long time to accomplish it, the consideration of the official method for determining moisture as compared with newer methods which might be developed for each kind of food or feeding stuff might be valuable.

INORGANIC PHOSPHORUS IN ANIMAL TISSUE[1].

By E. B. Forbes (Agricultural Experiment Station, Wooster, Ohio), *Referee on Organic and Inorganic Phosphorus in Foods, Feeding Stuffs and Drugs.*

Further study has been given the magnesia mixture method for inorganic phosphorus in animal tissue. The methods of extraction and precipitation used with flesh, blood and brain were those reported in 1914[2] with the exception of modifications hereinafter noted. The analyses which form the basis for this report were made by F. M. Beegle (Agricultural Experiment Station, Wooster, Ohio), who worked under the direction of the referee, and Byron McClelland (Bureau of Chemistry, Washington, D. C.). The first program of work was as indicated by the following schedule:

---

[1] Presented by H. C. Lythgoe.

[2] *J. Assoc. Official Agr. Chemists*, 1916, **1**: No. 4 (I), 562–80.

SCHEDULE OF ESTIMATIONS ON WATER-SOLUBLE INORGANIC PHOSPHORUS IN BLOOD AND BRAIN.

USE 10 CC. OF MAGNESIA MIXTURE; ALLOW TO STAND 2 DAYS:

Extract of samples as weighed.	Extract of samples as weighed plus phosphate solution[1].
A-1	B-1
A-2	B-2
A-3	B-3

USE 50 CC. OF MAGNESIA MIXTURE; ALLOW TO STAND 3 DAYS:

Extract of samples as weighed.	Extract of samples as weighed plus phosphate solution[1].
C-1	D-1
C-2	D-2
C-3	D-3

Tables 1 and 2 exhibit complete recovery of added phosphorus in blood with 10 cc. of magnesia mixture and two days standing. If 50 cc. of magnesia mixture are used and allowed to stand three days, the results

TABLE 1.

Inorganic phosphorus determinations in calf blood.

(Analyses by F. M. Beegle.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	PHOSPHORUS	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	PHOSPHORUS RECOVERED	
						MAGNESIUM PYROPHOSPHATE	PER CENT
		grams	*gram*	*per cent*	*gram*	*gram*	
10 cc. of magnesia mixture; stood 2 days.	A-1	38.5	0.0068	0.00492	.....	.....	.....
	A-2	39.8	0.0076	0.00532	.....	.....	.....
	A-3	35.5	0.0063	0.00494	.....	.....	.....
	Average	....	.....	0.00506	.....	.....	.....
10 cc. of magnesia mixture; stood 2 days.	B-1	37.2	0.0511	.....	0.0448	0.0445	.....
	B-2	35.3	0.0510	.....	0.0448	0.0448	.....
	B-3	41.9	0.0528	.....	0.0448	0.0454	.....
	Average	....	.....	.....	0.0448	0.0449	100.22
50 cc. of magnesia mixture; stood 3 days.	C-1	39.5	0.0089	0.00628	.....	.....	.....
	C-2	47.9	0.0107	0.00622	.....	.....	.....
	C-3	34.3	0.0084	0.00682	.....	.....	.....
	Average	....	.....	0.00644	.....	.....	.....
50 cc. of magnesia mixture; stood 3 days.	D-1	41.3	0.0536	.....	0.0448	0.0440	.....
	D-2	30.3	0.0512	.....	0.0448	0.0441	.....
	D-3	42.5	0.0546	.....	0.0448	0.0447	.....
	Average	....	.....	.....	0.0448	0.0443	98.88

[1] Include also blanks on the reagents and checks on the phosphate solution added.

are higher. Inorganic phosphorus apparently is split off, but complete recovery of added phosphorus is noted.

Table 3 indicates that the precipitation of inorganic phosphorus increases with the amount of magnesia mixture added and the length of time allowed for precipitation, probably through cleavage of organic compounds.

TABLE 2.

Inorganic phosphorus determinations in blood.

(Analyses by Byron McClelland.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	INORGANIC PHOSPHORUS	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	PHOSPHORUS RECOVERED	
						MAGNESIUM PYROPHOSPHATE	PER CENT
		grams	*gram*	*per cent*	*gram*	*gram*	
10 cc. of magnesia mixture; stood 2 days.	A-1	30.00	0.0063	0.00585	.....	.....	....
	A-2	30.00	0.0062	0.00575	.....	.....	....
	A-3	30.00	0.0060	0.00568	.....	.....	....
	Average	....	.....	0.00576	.....	.....	....
10 cc. of magnesia mixture; stood 2 days.	B-1	30.00	0.0650	.....	0.0583	0.0588	....
	B-2	30.00	0.0641	.....	0.0583	0.0579	....
	B-3	30.00	0.0642	.....	0.0583	0.0580	....
	Average	....	.....	.....	0.0583	0.0582	99.83
50 cc. of magnesia mixture; stood 3 days.	C-1	30.00	0.0077	0.00714	.....	.....	....
	C-2	30.00	0.0078	0.00724	.....	.....	....
	C-3	30.00	0.0074	0.00687	.....	.....	....
	Avergae	....	.....	0.00708	.....	.....	....
50 cc. of magnesia mixture; stood 3 days.	D-1	30.00	0.0628	.....	0.0555	0.0552	....
	D-2	30.00	0.0633	.....	0.0555	0.0557	....
	D-3	30.00	0.0629	.....	0.0555	0.0553	....
	Average	....	.....	.....	0.0555	0.0554	99.81

Table 4 indicates that precipitation is probably not complete with reduced time. No evidence is noted that the presence of added phosphate induced hydrolysis of organic compounds. Similar results were obtained with brain, Tables 5 and 6. The amount of inorganic phosphorus precipitated increased when 10 cc. of magnesia mixture in hot-water-ammonium-sulphate extracts of brain were used and the length of time increased, but when 50 cc. of magnesia mixture were used little increase was noted (Table 7).

The recovery of added phosphate is not quite so high on brain when only 10 cc. of magnesia mixture are used and the time shortened. The presence of phosphate solution does not appear to induce hydrolysis during extraction (Table 8). The time element is not so important on

TABLE 3.

Inorganic phosphorus in hot-water-ammonium-sulphate extract of blood.

(Analyses by F. M. Beegle.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	INORGANIC PHOSPHORUS
		grams	*gram*	*per cent*
Extract precipitated with 10 cc. of magnesia mixture and 25 cc. of ammonium hydrate; stood 2 days before filtering.	1	27.50	0.0017	0.00171
	2	30.80	0.0005	.....
	3	31.20	0.0020	0.00179
	Average	....	.....	0.00175
Extract precipitated with 10 cc. of magnesia mixture and 25 cc. of ammonium hydrate; stood 3 days before filtering.	4	30.80	0.0025	0.00227
	5	35.90	0.0037	0.00287
	6	35.10	0.0030	0.00239
	Average	....	.....	0.00251
Extract precipitated with 10 cc. of magnesia mixture and 25 cc. of ammonium hydrate; stood 4 days before filtering.	7	24.70	0.0008	.....
	8	29.00	0.0029	0.00279
	9	25.80	0.0024	0.00260
	Average	....	.....	0.00269
Extract precipitated with 50 cc. of magnesia mixture:				
Stood 2 days	10	33.70	0.0049	0.00407
Stood 3 days	11	36.70	0.0061	0.00463
Stood 4 days	12	31.10	0.0057	0.00511
	Average	....	.....	0.00460

TABLE 4.

Inorganic phosphorus in the hot-water-ammonium-sulphate extract of blood[1].

(Analyses by F. M. Beegle.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	INORGANIC PHOSPHORUS
		grams	*gram*	*per cent*
No phosphate solution added.	A-1	27.0	0.0010	0.00103
	A-2	42.1	0.0026	0.00172
	A-3	40.3	0.0011	0.00075
25 cc. of phosphate solution added to extract before precipitation.	B-1	38.7	0.0424	.....
	B-2	34.9	0.0403	.....
	B-3	34.0	0.0402	.....
25 cc. of phosphate solution added to sample before extraction.	C-1	33.2	0.0356	.....
	C-2	37.7	0.0425	.....
	C-3	33.9	0.0349	.....

[1] All samples were precipitated with 10 cc. magnesia mixture and allowed to stand overnight.

flesh as on blood, the extract being more stable. This is true whether 10 cc. or 50 cc. of magnesia mixture are used (Table 9).

Table 10 indicates that McClelland got complete recovery in three days on flesh and slightly less in two days.

Table 11 gives results for flesh similar to those obtained on blood and brain in Tables 4 and 8.

CONCLUSIONS.

Inorganic phosphorus estimations on flesh sustained previous work in showing 10 cc. of magnesia mixture to be sufficient for the precipitation of the phosphates in cold-water extracts from 10 to 12 gram samples; also, standing overnight was shown not to be sufficient time allowance for complete precipitation. In most of the work two days time for precipitation has been found sufficient, there being no difference in results from two, three and four days standing; but it is true that occasionally, as in McClelland's work (Table 10), three days standing seems to be necessary.

TABLE 5.

Inorganic phosphorus in calf brain.

(Analyses by F. M. Beegle.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	PHOSPHORUS	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	PHOSPHORUS RECOVERED	
						MAGNESIUM PYROPHOSPHATE	PER CENT
		grams	*gram*	*per cent*	*gram*	*gram*	
10 cc. of magnesia mixture; stood 2 days.	A-1	9.2074	0.0135	0.0409	.....	.....	.....
	A-2	8.7972	0.0118	0.0374	.....	.....	.....
	A-3	12.0259	0.0206	0.0477	.....	.....	.....
	Average	.....	.....	0.0453	.....	.....	.....
10 cc. of magnesia mixture; stood 2 days.	B-1	8.5200	0.0576	.....	0.0448	0.0446	.....
	B-2	10.8536	0.0645	.....	0.0448	0.0479	.....
	B-3	11.2700	0.0645	.....	0.0448	0.0473	.....
	Average	.....	.....	.....	0.0448	0.0466	104.02
50 cc. of magnesia mixture; stood 3 days.	C-1	9.0783	0.0201	0.0617	.....	.....	.....
	C-2	10.3188	0.0203	0.0548	.....	.....	.....
	C-3	8.7014	0.0166	0.0532	.....	.....	.....
	Average	.....	.....	0.0566	.....	.....	.....
50 cc. of magnesia mixture; stood 3 days.	D-1	7.9749	0.0614	.....	0.0448	0.0452	.....
	D-2	9.6137	0.0656	.....	0.0448	0.0461	.....
	D-3	10.6250	0.0680	.....	0.0448	0.0465	.....
	Average	.....	.....	.....	0.0448	0.0459	102.45

The amount of inorganic phosphorus precipitable from hot-water-ammonium-sulphate extracts of blood by the use of magnesia mixture and ammonia increases in proportion to the amount of magnesia mixture used and the length of time allowed for precipitation. The extract is clearly unstable, under these conditions, and the magnesia mixture method of inorganic phosphorus estimation is not applicable to blood.

If 50 cc. of magnesia mixture were used, the amount of inorganic phosphorus precipitable from hot-water-ammonium-sulphate extracts of brain, by the use of magnesia mixture and ammonia, was shown not to vary when two, three or four days time was allowed for precipitation. Two days time was shown to be sufficient for complete precipitation. Added phosphate was completely recovered, whether 10 cc. or 50 cc. of magnesia mixture were used in the precipitation, but the amount of inorganic phosphorus found in the sample was much greater when 50 cc. of magnesia mixture were used.

TABLE 6.

Inorganic phosphorus determinations in brain.

(Analyses by Byron McClelland.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	INORGANIC PHOSPHORUS	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	PHOSPHORUS RECOVERED	
						MAGNESIUM PYROPHOSPHATE	PER CENT
		grams	*gram*	*per cent*	*gram*	*gram*	
10 cc. of magnesia mixture; stood 2 days.	A-1	10.00	0.0200	0.0557	.....	.....	.....
	A-2	10.00	0.0198	0.0551	.....	.....	.....
	A-3	10.00	0.0197	0.0548	.....	.....	.....
	Average	....	.....	0.0552	.....	.....	.....
10 cc. of magnesia mixture; stood 2 days.	B-1	10.00	0.0726	.....	0.0528	0.0528	.....
	B-2	10.00	0.0729	.....	0.0528	0.0531	.....
	B-3	10.00	0.0723	.....	0.0528	0.0525	.....
	Average	....	.....	.....	0.0528	0.0528	100.00
50 cc. of magnesia mixture; stood 3 days.	C-1	10.00	0.0222	0.0618	.....	.....	.....
	C-2	10.00	0.0224	0.0624	.....	.....	.....
	C-3	10.00	0.0227	0.0632	.....	.....	.....
	Average	....	.....	0.0628	.....	.....	.....
50 cc. of magnesia mixture; stood 3 days.	D-1	10.00	0.0714	.....	0.0494	0.0490	.....
	D-2	10.00	0.0717	.....	0.0494	0.0493	.....
	D-3	10.00	0.0711	.....	0.0494	0.0487	.....
	Average	....	.....	.....	0.0494	0.0490	99.19

TABLE 7.

Inorganic phosphorus in hot-water-ammonium-sulphate extract of steer brain.

(Analyses by F. M. Beegle.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	INORGANIC PHOSPHORUS
		grams	*gram*	*per cent*
10 cc. of magnesia mixture and 25 cc. of ammonium hydrate; stood 2 days before filtering.	1	10.6511	0.0109	0.0285
	2	10.9059	0.0137	0.0350
	3	11.9099	0.0179	0.0419
10 cc. of magnesia mixture and 25 cc. of ammonium hydrate; stood 3 days before filtering.	4	9.7376	0.0136	0.0389
	5	10.4890	0.0161	0.0428
	6	10.9132	0.0148	0.0378
10 cc. of magnesia mixture and 25 cc. of ammonium hydrate; stood 4 days before filtering.	7	13.0308	0.0204	0.0436
	8	10.5708	0.0175	0.0462
	9	11.4914	0.0194	0.0471
50 cc. of magesia mixture:				
Stood 2 days	10	10.3200	0.0198	0.0535
Stood 3 days	11	8.9327	0.0177	0.0552
Stood 4 days	12	9.4823	0.0187	0.0549

TABLE 8.

Inorganic phosphorus in hot-water-ammonium-sulphate in extract of brain.

(Analyses by F. M. Beegle.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	INORGANIC PHOSPHORUS	PHOSPHORUS RECOVERED	
					MAGNESIUM PYROPHOSPHATE	PER CENT
		grams	*gram*	*per cent*	*gram*	
10 cc. of magnesia mixture; stood overnight.	A-1	9.0500	0.0178	0.0548	.....	....
	A-2	11.3821	0.0223	0.0546	.....	....
	A-3	9.0038	0.0164	0.0508	.....	....
	Average	.....	.....	0.0534	.....	....
25 cc. of phosphate solution added to extract before precipitation.	B-1	10.7052	0.0655	.....	0.0450	....
	B-2	11.2060	0.0693	.....	0.0478	....
	B-3	10.1177	0.0622	.....	0.0428	....
	Average	.....	.....	.....	0.0452	96.79
25 cc. of phosphate solution added to sample before extraction.	C-1	9.7845	0.0653	.....	0.0466	....
	C-2	11.4200	0.0658	.....	0.0439	....
	C-3	12.1604	0.0706	.....	0.0473	....
	Average	.....	.....	.....	0.0459	98.29

In the light of present information, then, we must consider that a definite fraction of the organic phosphorus of brain is hydrolyzed in hot-water-ammonium-sulphate extracts by the addition of 50 cc. of magnesia mixture and 25 cc. of ammonium hydrate. The magnesia mixture method for inorganic phosphorus estimation, therefore, can not be approved for use on brain without further study and modification.

It seems possible that the use of graduated amounts of magnesia mixture in the precipitation of extracts of brain might demonstrate that, within certain ranges of variation in the amount of this reagent used, complete recovery of added phosphorus might be demonstrated without there being variations in the amounts of inorganic phosphorus precipitated from the sample.

TABLE 9.

Inorganic phosphorus in cold water extract of flesh.

(Analyses by F. M. Beegle.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	INORGANIC PHOSPHORUS
		grams	*gram*	*per cent*
Extract precipitated with 10 cc. of magnesia mixture and 25 cc. of ammonium hydrate; stood 2 days before filtering.	1	10.1577	0.0571	0.1566
	2	8.8276	0.0500	0.1578
	3	10.8487	0.0609	0.1564
	Average	.....	.....	0.1569
Extract precipitated with 10 cc of magnesia mixture and 25 cc. of ammonium hydrate; stood 3 days before filtering.	4	12.1040	0.0679	0.1563
	5	9.3100	0.0628	0.1879
	6	9.1685	0.0514	0.1562
	Average (4 and 6)	.....	.....	0.1563
Extract precipitated with 10 cc. of magnesia mixture and 25 cc. of ammonium hydrate; stood 4 days before filtering.	7	10.3800	0.0584	0.1567
	8	11.5615	0.0649	0.1563
	9	10.6850	0.0592	0.1543
	Average (7 and 8)	.....	.....	0.1565
Precipitated with 50 cc. of magnesia mixture:				
Stood 2 days	10	12.4419	0.0707	0.1583
Stood 3 days	11	12.2478	0.0695	0.1581
Stood 4 days	12	12.0138	0.0681	0.1579
	Average	.....	.....	0.1581

TABLE 10.

Inorganic phosphorus determinations on lean meat in pork chops.

(Analyses by Byron McClelland.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	INORGANIC PHOSPHORUS	PHOSPHORUS ADDED AS MAGNESIUM PYROPHOSPHATE	ADDED PHOSPHORUS RECOVERED AS MAGNESIUM PYROPHOSPHATE
		grams	*gram*	*per cent*	*gram*	*per cent*
No phosphate added; stood 3 days before filtration.	A-1	10	0.0419	0.1167	.....	.....
	A-2	10	0.0424	0.1180	.....	.....
Phosphate added; stood 3 days before filtration.	B-1	10	0.1077	.....	0.0658	99.54
	B-2	10	0.1088	.....	0.0658	101.21
No phosphate added; stood 2 days before filtration.	C-1	10	0.0442	0.1231	.....	.....
	C-2	10	0.0444	0.1236	.....	.....
Phosphate added; stood 2 days before filtration.	D-1	10	0.1084	.....	0.0658	97.42
	D-2	10	0.1090	.....	0.0658	98.33

TABLE 11.

Inorganic phosphorus in the cold water extract of flesh.

(Analyses by F. M. Beegle.)

TREATMENT	SAMPLE NUMBER	WEIGHT OF SAMPLE	WEIGHT OF MAGNESIUM PYROPHOSPHATE MINUS BLANK	INORGANIC PHOSPHORUS	PHOSPHORUS RECOVERED	
					MAGNESIUM PYROPHOSPHATE	PER CENT.
		grams	*gram*	*per cent*	*gram*	
All samples precipitated with 10 cc. of magnesia mixture and allowed to stand overnight.	A-1	10.2200	0.0531	0.1447	.....	.....
	A-2	11.8576	0.0618	0.1452	.....	.....
	A-3	14.2849	0.0741	0.1446	.....	.....
	Average	.....	.....	0.1448	.....	.....
25 cc. of phosphate solution added to extract before precipitation.	B-1	14.2843	0.1184	.....	0.0442	.....
	B-2	11.5875	0.1051	.....	0.0449	.....
	B-3	13.8000	0.1153	.....	0.0436	.....
	Average	.....	.....	.....	0.0442	94.647
25 cc. of phosphate solution added to sample before extraction.	C-1	12.9650	0.1111	.....	0.0437	.....
	C-2	13.8850	0.1161	.....	0.0439	.....
	C-3	11.2495	0.1013	.....	0.0428	.....
	Average	.....	.....	.....	0.0435	93.148

RECOMMENDATIONS.

It is recommended—

(1) That the magnesia mixture method for the estimation of water-soluble inorganic phosphorus in flesh be adopted as an official method, with one minor change of detail, in the interest of economy of reagents, namely, that the amount of magnesia mixture used in extracts from 10 to 12 gram samples be reduced from 50 cc. to 10 cc.

(2) That further work be done with the magnesia mixture method on brain.

(3) That further work with blood be conducted, not on the whole blood, but on the plasma.

No report was made by the referee on the separation of nitrogenous substances.

REPORT ON THE SEPARATION OF NITROGENOUS SUBSTANCES IN MILK AND CHEESE.

By LEROY S. PALMER[1] (Agricultural Experiment Station, Columbia, Mo.), *Associate Referee.*

Work has been begun along three lines. (1) As stated last year, 8 to 10 per cent of the total true protein of fresh milk is not recovered either as casein or as heat-coagulable proteins by the methods which this association recognizes. The residual proteins may be recovered, however, by addition of Almen's tannic acid solution to the filtrate obtained from the heat-coagulable proteins. The origin and character of these residual proteins, as present in fresh milk, should be studied, particularly in view of the fact that it is this portion of the milk which increases to such a great extent as protein decomposition progresses in old milk.

(2) Preliminary studies indicate that the addition of 0.3 cc. of 10 per cent acetic acid to the neutral casein filtrate, as recommended by the provisional method for albumin, may not be enough to recover the maximum amount of heat-coagulable proteins.

(3) Another question being studied is the character and proportion of the heat-coagulable protein which recent investigation[2] has found to be in colloidal solution in the milk like the casein, or which, at any rate, is retained with the casein when milk is filtered through the Pasteur-Chamberland filter.

Such studies are necessary before methods of analysis can be recommended for cooperative study by the association.

---

[1] Present address, University of Minnesota, University Farm, St. Paul, Minn.

[2] Van Slyke and Bosworth. N. Y. Agr. Exp. Sta. *Tech. Bull.* 39, (1914), 7.

RECOMMENDATION.

It is recommended—

(1) That studies be continued leading to the adoption of methods for the determination of the non-casein proteins and the products of protein decomposition in milk.

ORIGIN OF THE NEUTRALIZATION PRECIPITATE OF COWS' MILK.

By LEROY S. PALMER[1] (Agricultural Experiment Station, Columbia, Mo.).

The author has shown[2] that the so-called neutralization precipitate obtained on neutralizing the filtrate obtained from the acetic acid precipitation of the casein from cows' milk was composed almost entirely of di- and tricalcium phosphates. Recent work by Van Slyke and Bosworth[3] offers a very satisfactory explanation of the origin of this precipitate, and at the same time clears up several other features of the work which were in doubt at the time the first paper was prepared.

The work of these investigators shows that the di- and tricalcium phosphates found in the neutralization precipitate are the result of several chemical reactions between the calcium and phosphorus compounds normal to milk and the calcium acetate which is formed as the result of the action of the added acetic acid upon (a) the calcium combined with the casein and (b) the calcium chlorid of the milk serum. The sodium hydroxid added to bring about the precipitation of the neutralization precipitate is also involved. The salts entering into the reactions to form the di- and tricalcium phosphates are calcium phosphate, potassium phosphate and calcium acetate. The presence of monomagnesium phosphate in milk, as shown by Van Slyke and Bosworth, makes probable the presence of some magnesium phosphate in the neutralization precipitate.

The reactions which enter into the formation of the neutralization precipitate may be expressed as follows:

(1) $CaH_4P_2O_8+CaC_4H_6O_4=2\ CaHPO_4+2\ C_2H_4O_2$.

(2) $CaC_4H_6O_4+2\ NaOH=Ca(OH)_2+2\ NaC_2H_3O_2$.

(3) $2\ CaHPO_4+Ca(OH)_2=Ca_3P_2O_8+2\ H_2O$.

(4) $3\ CaC_4H_6O_4+12\ K_2HPO_4+12\ NaOH=Ca_3P_2O_8+6\ K_3PO_4+6\ KC_2H_3O_2+4\ Na_3PO_4+12\ H_2O$.

As pointed out in my previous paper, casein precipitated by rennet yields a filtrate which does not show the neutralization precipitate. This result also becomes clear in view of studies by Bosworth and Van Slyke[3]. They have found that the paracasein thrown down by rennet

[1] Present address, University of Minnesota, University Farm, St. Paul, Minn.
[2] *Assoc. Official Agr. Chemists*, 1916, 2: No. 1 (I), 4–8.
[3] N. Y. Agr. Exp. Sta. *Tech. Bull.* 39 (1914), 3–17.
[4] Ibid., 37 (1914), 7–10.

contains the calcium in its molecule like the casein thrown down by acid, and also carries down with it the dicalcium phosphate of the colloidal part of the milk. Rennet coagulation leaves no calcium phosphate in the serum, which accounts for the failure of a neutralization precipitate to appear on the addition of sodium hydroxid to the acidified serum. Recent tests by the author have demonstrated, however, that other phosphates in the serum can be detected readily by the addition of calcium acetate and a repetition of the neutralization, when the characteristic precipitate appears.

The failure of the protein precipitated by rennet to yield a neutralization precipitate on proper treatment is still unexplained.

Paracasein was prepared from skim-milk and thoroughly washed with water until it had a greenish white appearance. Portions were dissolved in acetic acid and ammonium hydroxid, respectively. In the case of the acid solution, a reprecipitation of the protein with sodium hydroxid yielded a filtrate showing the presence of calcium on the addition of ammonium oxalate. This was to be expected from the action of the acetic acid on the calcium combined with the paracasein. There was no evidence of a neutralization precipitate, however, although one would expect that any dicalcium phosphate carried down with the paracasein would be converted into soluble phosphate by the acetic acid and reappear on neutralization. Similarly, it would be expected, in the case of the alkaline solution of paracasein, that the dicalcium phosphate held by the paracasein would be converted into tricalcium phosphate; but this should be changed into the soluble phosphate by the acetic acid and reappear as neutralization precipitate on the addition of sodium hydroxid.

The only explanation at present available for these results is that the purification of the paracasein was not sufficient to remove enough of the dicalcium phosphate held mechanically to assure its reappearance as a neutralization precipitate.

PROGRESS REPORT ON THE SEPARATION OF NITROGENOUS SUBSTANCES IN MEAT PRODUCTS.

By P. F. Trowbridge[1] (Agricultural Experiment Station, Columbia, Mo.), *Associate Referee.*

The work is being done by Walter E. Thrun (Agricultural Experiment Station, Columbia, Mo.), the purpose of which is to study the effect of age and condition of the animal upon the composition of the flesh.

Ten pounds of flesh are extracted with cold water until the filtrate no longer gives the Biuret reaction. The extract is concentrated by

[1] Present address, Agricultural Experiment Station, Agricultural College, N. Dak.

heat on a water bath and the coagulable proteins separated by washing. Three main samples of the flesh are thus obtained: the cold water insoluble; the cold water soluble coagulable; and the extract. The cold water insoluble is extracted with alcohol and ether and the alcohol-ether extract examined for lecithin and other nitrogenous compounds. The purine nitrogen[1] in the residue is determined, and also the amino nitrogen. It is then run for Van Slyke numbers. Tryptophane will also be determined according to the method of Annie Homer[2], also tyrosine according to the method of Plimmer and Eaves[3]. The aspartic and glutaminic acids will be determined according to the method of Foreman[4]. The coagulable proteins are to be run in the same way as the insoluble residue, except that the purine nitrogen will not have to be determined. The extractives are concentrated to a sirup, but the exact method of handling has not been completely worked out. The samples have been prepared and some of the Van Slyke determinations made, as have many other preliminary determinations and tests.

RECOMMENDATION.

It is recommended—

(1) That these investigations be continued.

REPORT ON TESTING CHEMICAL REAGENTS.

By C. O. Ewing[5] (Bureau of Chemistry, Washington, D. C.), *Referee.*

The situation with regard to chemical reagents during the past year has been abnormal. Efforts on the part of users and manufacturers should soon clear up difficulties which have been met in obtaining some reagents of a satisfactory quality.

The cooperative work of the year consisted in testing the method for the determination of alcohol in pharmaceutical preparations as outlined in last year's report. The method will provide for almost all interfering substances except phenol. When it is present the following modification is used[6]:

> After the first distillate has been shaken out twice with petroleum ether, draw off the lower alcoholic salt solution into a 200 mil flask, add bromin water to slight excess as shown by a brownish color. Then add a crystal of sodium thiosulphate to remove the excess of bromin and sufficient 50% sodium hydroxid solution to dissolve the precipitated tri-brom-phenol and distil as usual.

---

[1] Hall. The Purine Bodies of Food Stuffs. 2nd ed. rev., 1903.
[2] *J. Biol. Chem.*, 1915, **22**: 369–89.
[3] *Biochem. J.*, 1913, **7**: 297–310.
[4] Ibid., 1914, **8**: 463.
[5] Present address, United Drug Company, Boston, Mass.
[6] *J. Ind. Eng. Chem.*, 1916, **8**: 240–1.

Only two collaborators reported results, and these were not sufficient to justify any positive conclusions as to the general applicability of the method.

RECOMMENDATIONS.

It is recommended—

(1) That work on the determination of alcohol in pharmaceutical preparations be continued.

(2) That the method for the determination of the strength of acetic anhydrid as outlined in this year's report be studied cooperatively.

(3) That work on tests of purity for immiscible organic solvents be undertaken.

The association adjourned at 12.55 a. m. to reconvene at 1.30 p. m.

A. HUGH BRYAN.

The death of this well-known food chemist came as a shock to his many friends, the chemical world and the sugar industry at large. His loss is the more keenly felt because death claimed him in the very midst of his life's task at the age of forty-six years. Mr. Bryan died at his home in Montclair, N. J., on January 19, 1920, after only a brief illness of influenza, followed by a complication of acute Bright's disease and pneumonia.

Mr. Bryan was born in Indianapolis on July 27, 1874. After graduating from the public and high schools of his native city he entered Purdue University, from which he received the degrees of B. S. in 1898, A. C. in 1899, and M. S. in 1900. Mr. Bryan's first position was that of assistant chemist at the Indiana Agricultural Experiment Station, where he remained until 1900, when he became chemist for the American Beet Sugar Company of Colorado. In 1907 he resigned his position with the American Beet Sugar Company to accept an appointment in the Bureau of Chemistry as a sugar chemist. He was made Chief of the Sugar Laboratory of the Bureau of Chemistry in 1909, which position he held until 1913, when he resigned to accept his last position as supervising chemist for Arbuckle Brothers of New York City.

There probably was no chemist who was in more intimate touch with the various sides of our American sugar industry than Mr. Bryan. His practical experience brought him into close relations with the beet sugar industry of the West, the cane sugar and cane sirup industry of the South, the sorghum sirup industry of the Central States, the maple sugar and maple sirup industry of the North, and the refining industry of the East. Fully aware of the important role of chemistry in the advancement of all of these branches of sugar chemistry, he was a constant contributor to the chemical literature upon these subjects. His writings comprise a large number of bulletins, circulars and articles upon the subjects of sugar beet, cane, sorghum, maple sirups, honey, etc. He was preparing at the time of his death a book upon the chemistry of coffee, and it is greatly to be regretted that he did not live to complete this work.

Mr. Bryan was at numerous times, and as late as 1919, a referee for the Association of Official Agricultural Chemists, and his various reports upon methods of sugar analysis to this association constitute an important part of its published proceedings. Many of his suggestions have been incorporated in the official methods of analysis.

In addition to being a member of the Association of Official Agricultural Chemists, Mr. Bryan was a member of the American Chemical Society, the International Commission for Uniform Methods of Sugar Analysis, the Indiana Academy of Sciences and the Washington Academy of Sciences. He was deeply interested in the recent establishment of the Society of American Sugar Chemists and Technologists.

Only those who have lived in close companionship with Mr. Bryan can speak of the fullness and accuracy of his knowledge, which was always at the service of those who constantly called upon him for advice.

The many friends who have enjoyed the hospitality of Mr. and Mrs. Bryan will always remember the happiness of their home life. The sympathy of everyone goes out to the faithful wife and son in their bereavement.

R. E. Doolittle.

GLUES USED IN AIRPLANE PARTS[1].

Report No. 66, entitled "Glues Used in Airplane Parts", embodies the results of experimental research on the glues used in the manufacture of wooden airplane parts. The experiments were conducted by the Forest Products Laboratory of the United States Forest Service.

The report first contains a general statement descriptive of the different kinds of glues used. This statement is followed by detailed descriptions of the following kinds of glues: Animal glues, liquid glues, casein glues, blood albumin glues, and vegetable glues. The detailed discussion includes the description of the manufacture of each type, giving the physical properties, the use of each type of glue, including the proper methods of application, and the proper pressure and temperature required to obtain the best results. Following the detailed discussion of each type is a list of references.

A comparison of the different types of glues is next given in tabular form, the table containing the following information: Source, cost, spread, mixing, application, temperature of press, strength, water resistance, staining, and the use of each type in wood-working.

The physical tests described in this paper include block shear tests and ply shear tests. Tests were also made to describe the water resistant properties of the glues, keeping quality, odor, jelly strength, viscosity, and other physical properties.

A copy of Report No. 66, entitled "Glues Used in Airplane Parts", may be obtained upon request from the National Advisory Committee for Aeronautics, Washington, D. C.

INDUSTRIAL USES OF GLYCEROL.

A prominent manufacturer has recently established a fellowship at the Mellon Institute of Industrial Research, Pittsburgh, Pa., for the purpose of extending the industrial uses of glycerol. It is expected that this investigation will be centered primarily on the use of glycerol to replace alcohol in flavoring extracts.

The Mellon Institute is an endowed institution devoted to scientific research and its application to the industries. Its investigations are conducted by means of fellowships, and in such a manner that they are not affected by any financial or private interest. It is hoped that the results of this glycerol fellowship may be brought to the attention of industrialists by cooperation with various associations.

---

[1] Abs. of Rept. 66, National Advisory Committee for Aeronautics.

FIRST DAY.

MONDAY—AFTERNOON SESSION.

The appointment of the following committees was announced by the president:

Auditing committee: J. P. Street, of Connecticut; B. B. Ross, of Alabama; and C. B. Lipman, of California.

Committee on nominations: C. C. McDonnell, of Washington, D. C.; G. S. Fraps, of Texas; and B. L. Hartwell, of Rhode Island.

Committee on resolutions: William Frear, of Pennsylvania; L. L. Van Slyke, of New York; and W. A. Withers, of North Carolina.

Committee to invite the Secretary of Agriculture to address the convention: C. H. Jones, of Vermont; P. F. Trowbridge, of Missouri; and W. A. Withers, of North Carolina.

REPORT ON PHOSPHORIC ACID.

By W. J. Jones, jr. (State Chemist Department, La Fayette, Ind.), *Referee*, and C. S. Lykes (Clemson Agricultural College, Clemson College, S. C.), *Associate Referee.*

Details of the proposed plan for the investigation of the determination of reverted phosphoric acid are contained in the report of the associate referee for 1915[1]. This report is one of progress and not for permanent deductions or conclusions.

Since the basis of comparison at the present time is a series of results obtained by the use of ammonium citrate solutions, specific gravity 1.09, the first subject for investigation was the study of the methods proposed for preparing neutral ammonium citrate solution, their action and that of proposed substitutes on the phosphoric acid in fertilizers as compared with a solution of 1.09 specific gravity prepared from the neutral triammonium citrate salt.

---

[1] W. J. Jones, jr. *J. Assoc. Official Agr. Chemists*, 1917, 3: 97.

SOLUTIONS STUDIED.

The following solutions, prepared according to the instructions of the various author ties, were studied:

(1) Official method using corallin as an indicator[1].

(2) Optional method using alcoholic calcium chlorid and cochineal[2].

(3) Hand's method using azolitmin as an indicator[3].

(4) Solution 1.09 specific gravity from triammonium citrate salt (Baker & Adam son's analyzed ammonium citrate, C. P.).

(5) Patten's titration method using phenolphthalein as the indicator in the presen of neutral formaldehyde[4].

(6) Hildebrand's method using rosolic acid as the indicator[5].

(7) Rudnick's method with N/10 citric acid[6].

(8) Bosworth's method with sodium citrate[7].

PREPARATION OF SOLUTIONS.

Ammonium citrate.—With the exception of the solution from the triammoniu citrate salt, the solutions were prepared from Pfizer's commercial citric acid and fro C. P. ammonia.

Citric acid.—Analyzed citric acid, C. P., was used and the strength of the solutio determined by titrating with N/10 potassium hydroxid, using phenolphthalein a indicator.

Sodium citrate.—This solution was prepared by dissolving 305.6086 grams of analyze sodium citrate, C. P., (this amount being equivalent to the triammonium citrate in solution of 1.09 specific gravity) and making up to 1 liter. Specific gravity at 20°C 1.1726.

Redistilled rain water was used for all the solutions.

METHODS EMPLOYED.

The specific gravity was determined by means of a pycnometer.

AMMONIA.

Twenty-five cc. of the citrate solution at 20°C. were made up to 250 cc., and 25 cc equivalent to 2.5 cc. of original solution, distilled with 3–5 grams of magnesium oxi into N/2 acid, the excess acid being titrated with N/10 potassium hydroxid, usin cochineal as an indicator.

In Patten's method ammonia is determined by making 50 cc. up to 250 cc. an distilling 5 cc., equivalent to 1 cc. of original solution, with magnesium oxid. Deter minations are therefore reported by both methods on this solution.

CITRIC ACID.

Fifty cc. of the solution were made up to 250 cc. and 5 cc., equivalent to 1 cc. of th original solution, were titrated with N/10 potassium hydroxid in the presence of neutra formaldehyde, using phenolphthalein as an indicator.

---

[1] U. S. Bur. Chem. Bull. **107**, rev.: 1.
[2] *Assoc. Official Agr. Chemists, Methods*, 1916, 4.
[3] U. S. Bur. Chem. Circ. **52**: 1.
[4] *J. Ind. Eng. Chem.*, 1913, **5**: 567.
[5] *Ibid.*, 1914, **6**: 577.
[6] *Ibid.*, 1914, **6**: 486.
[7] *Ibid.*, 1914, **6**: 277.

SOLVENT ACTION OF SOLUTIONS ON PHOSPHORIC ACID IN FERTILIZERS.

DESCRIPTION OF SAMPLES.

In selecting samples for determining the action of the various solutions on phosphoric acid, 24 samples, of which 22 were on general sale and representative of the products of 8 manufacturers doing an interstate business, were selected. The other 2 samples consisted of tricalcium phosphate and a mixture of the excess inspection samples from the mill room. All samples were ground to pass 100 mesh.

TABLE 1.

Comparison of various methods of preparation of solution of ammonium citrate.

(Analyst, R. B. Deemer, State Chemist Department, La Fayette, Ind.)

SOLUTION	SPECIFIC GRAVITY AT 20°C.	GRAMS PER LITER		RATIO AMMONIA TO CITRIC ACID
		Ammonia	Citric acid	
(1) Corallin	1.09005	43.33	165.82	1–3.826
(2) Optional. Cochineal	1.09007	43.64	166.01	1–3.788
(3) Hand. Azolitmin	1.09009	43.40	168.12	1–3.873
(4) Triammonium citrate salt solution	1.09003	43.73	165.11	1–3.776[a]
Triammonium citrate salt[b]	------	----	-----	1–3.777[b]
(5) Patten. Formaldehyde and phenolphthalein, 1 cc. for titrations	1.09002	44.08	165.81	1–3.761
2.5 cc. for titrations	------	43.75	165.81	1–3.789
(6) Hildebrand. Rosolic acid[c]	1.09004	44.37	165.92	1–3.739

SOLUTION	NEUTRALITY				
	Corallin	Alcoholic calcium chlorid and cochineal	Hand azolitmin	Patten formaldehyde and phenolphthalein	Hildebrand rosolic acid[d]
(1) Corallin	Neutral	Acid	Neutral	------	Acid
(2) Optional. Cochineal	Alkaline	Neutral	Neutral	------	Acid
(3) Hand. Azolitmin	------	Acid	Neutral	------	Acid
(4) Triammonium citrate salt solution	Alkaline	Neutral	Neutral	------	Acid
Triammonium citrate salt[b]	Alkaline	Neutral	Neutral	------	------
(5) Patten. Formaldehyde and phenolphthalein, 1 cc. for titrations	Alkaline	Alkaline	Neutral	Neutral	Acid
2.5 cc. for titrations	------	------	------	------	------
(6) Hildebrand. Rosolic acid[c]	------	------	------	------	Neutral

[a] Theory 1–3.7597.

[b] Twenty-five grams of the salt were made up to 250 cc. and ammonia and citric acid determined as in other solutions.

[c] Solution gave strong odor of ammonia. Moist red litmus paper suspended in calorimeter tube rapidly changed to blue color.

[d] True rosolic acid. (The inner anhydrid of α4, 4′, 4″,-tetrahydroxy-3-methyl-triphenylmethane.)

DETERMINATION OF INSOLUBLE PHOSPHORIC ACID.

Digestion.—The official method for digesting in citrate solution was followed in detail. Difference due to variation in agitation was eliminated by the use of Huston's Agitating Machine[1], each flask making 2 complete revolutions per minute.

SOLUTIONS.

Solutions for the determination of total and insoluble phosphoric acid were made by the sulphuric acid, mercuric oxid method and the determinations of phosphoric acid by the gravimetric method. All solutions and determinations were in duplicate with triplicates in case of disagreement.

TABLE 2.

Description and analyses of samples.

SAMPLE NUMBER	DESCRIPTION	NITROGEN (N)	POTASH SOLUBLE IN WATER	WATER-SOLUBLE PHOSPHORIC ACID (P_2O_5)	TOTAL PHOSPHORIC ACID (P_2O_5)
		per cent	*per cent*	*per cent*	*per cent*
3	Complete	1.0	3.1	3.99	19.29
4	Complete	1.5	2.3	4.20	10.65
5	Complete	0.9	2.7	7.39	13.64
7	Complete	1.6	2.3	1.10	10.14
10	Complete	0.9	2.9	4.63	15.94
11	Complete	0.3	3.5	4.52	18.53
14	Complete	0.9	6.9	1.92	7.26
15	Complete	1.5	2.0	3.95	9.82
30	Complete	1.0	3.2	8.39	13.36
34	Complete	2.6	1.6	6.82	12.13
40	Complete	1.0	1.0	1.59	9.57
43	Mixture of inspection samples	1.2	2.4	4.81	10.90
20	Acid phosphate	---	---	13.91	19.67
22	Acid phosphate	---	---	10.03	19.31
23	Acid phosphate	---	---	12.06	19.19
39	Acid phosphate	---	---	9.26	17.70
45	Acid phosphate, Florida	---	---	10.68	17.27
41	Precipitated bone	---	---	-----	38.61
18	Tankage	6.3	---	-----	14.16
24	Raw bone	4.1	---	-----	25.70
26	Ammoniated bone	2.6	---	-----	21.27
33	Raw bone	4.1	---	-----	22.12
47	Rock phosphate	---	---	-----	31.24
48	Tricalcium phosphate, C. P.	---	---	-----	41.89

COMMENTS BY ANALYST, R. B. DEEMER.

Corallin.—This indicator, while extremely sensitive in water standard to acid and alkali, loses its sensitiveness when added to an ammonium citrate solution, and calculations based on titrations were found to be incorrect. The use of this method in determining the neutrality of citrate solutions seems to be more or less guess work.

[1] H. W. Wiley. Principles and Practice of Agricultural Analysis. 2nd ed., 1908, 2: 117.

Hand's azolitmin.—This indicator[1] did not appear to be sensitive to less than 2 cc. of N/10 ammonia when used in the presence of 5 cc. of ammonium citrate solution.

Optional method.—The indicator used in this method is very sensitive, readily reacting to a drop of N/10 alkali or acid.

(*Referee.*—This method, having been in constant use in this department for 25 years, the analysts are undoubtedly more expert in its manipulation.)

Patten's method.—Patten, while stating that neutral formaldehyde is required for use in the titration of citric acid, makes no mention of how this is to be obtained. Formaldehyde which is neutralized in the cold with N/10 alkali shows an acid reaction when used under the conditions imposed by this method—that is, in a solution brought to boiling.

The small aliquot (1 cc.) used in this method necessitates the multiplying of the working error by 1000, in placing results upon a liter basis.

Another point that may be mentioned is the fact that in preparing large amounts of citrate (30 liters, as we usually do) to determine accurately the volume and calculate the amount of ammonium hydroxid to add is quite impracticable.

Hildebrand's method.—The solution prepared by this method gave off an appreciable odor of ammonia and quickly turned red litmus paper suspended in the neck of the bottle to blue.

Difficulty was experienced in filtering and washing the digestions of tricalcium phosphate with the exception of those in citric acid and sodium citrate. All digestions with sodium citrate of samples containing animal by-products were difficult to filter and wash.

Hirsh funnels were used in filtering all insolubles.

TENTATIVE CONCLUSIONS.

(1) Theoretical composition and ratios are not to be expected from solutions prepared according to official directions when a commercial salt, which may or may not contain impurities, is the basis of the solution.

(2) Owing to the small aliquot taken, the method for estimating citric acid greatly multiplies the working error.

(3) The results reported are not sufficient to justify permanent deductions but indicate:

(a) That the methods studied for the preparation of neutral ammonium citrate do not give a neutral solution, but that two, optional and Patten's, are slightly acid; two, corallin and Hand's, appreciably acid, and one, Hildebrand's, appreciably alkaline when compared with a solution of triammonium citrate salt, specific gravity 1.09.

(b) That of the solutions reported, two—optional and Patten's—are the more nearly neutral ammonium citrate and that in the results reported the former is more consistent in its variations.

(c) That the ammonia citric acid ratio is not necessarily the controlling factor in results obtained.

---

[1] Prepared according to Cohn. Indicators and Test-Papers. 2nd ed. 1902, 30.

TABLE

Description of samples and

(Analyst,

SAMPLE NUMBER	TRIAMMONIUM CITRATE SALT STANDARD	CORALLIN		OPTIONAL		HAND		PATTEN		HILDEBRAND	
	Reverted phosphoric acid (P_2O_5)	Reverted phosphoric acid (P_2O_5)	Difference	Reverted phosphoric acid (P_2O_5)	Difference	Reverted phosphoric acid (P_2O_5)	Difference	Reverted phosphoric acid (P_2O_5)	Difference	Reverted phosphoric acid (P_2O_5)	Difference
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
3	9.67	12.43	+2.76	9.07	−0.60	11.70	+2.03	8.21	−1.46	7.90	−1.77
4	4.13	4.53	+0.40	3.89	−0.24	4.65	+0.52	4.00	−0.13	3.81	−0.34
5	5.46	5.55	+0.09	5.26	−0.20	5.38	−0.08	5.41	−0.05	5.12	−0.34
7	6.90	7.10	+0.20	6.70	−0.20	7.22	+0.32	6.84	−0.06	6.60	−0.30
10	7.17	7.21	+0.04	6.97	−0.20	7.16	−0.01	1.06	−0.10	6.92	−0.25
11	6.69	6.72	+0.03	6.50	−0.19	6.83	+0.14	6.77	+0.08	6.60	−0.09
14	4.17	4.38	+0.21	3.94	−0.23	4.45	+0.28	4.18	+0.01	3.81	−0.36
15	3.82	4.22	+0.40	3.74	−0.08	4.40	+0.58	3.93	+0.11	3.78	−0.05
30	3.81	3.82	+0.01	3.87	+0.06	3.73	−0.08	3.75	−0.06	3.89	+0.08
34	3.59	3.52	−0.07	3.55	−0.04	3.59	±	3.49	−0.10	3.52	−0.07
40	6.77	6.77	±	6.74	−0.03	6.82	+0.05	6.72	−0.05	6.73	−0.04
43	4.03	4.11	+0.08	3.96	−0.07	4.04	+0.01	4.09	+0.06	3.92	−0.11
20	5.74	5.66	−0.08	5.57	−0.17	5.58	−0.17	5.79	±	5.66	−0.08
22	7.96	7.93	−0.03	7.89	−0.07	7.95	−0.01	8.07	−0.11	7.98	+0.02
23	5.58	5.63	+0.05	5.62	+0.04	5.76	+0.18	5.49	−0.09	5.65	+0.07
39	6.80	6.50	−0.30	6.72	−0.08	6.90	+0.10	6.67	−0.13	6.57	−0.23
45	6.45	6.36	−0.09	6.34	−0.11	6.39	−0.06	6.38	−0.07	6.40	−0.05
41	24.42	24.74	+0.32	22.33	−2.09	24.86	+0.44	22.58	−1.84	21.42	−3.00
18	9.25	9.14	−0.11	7.78	−1.47	9.41	+0.16	8.06	−1.19	6.58	−2.67
24	13.19	13.27	+0.08	12.10	−1.09	13.66	+0.47	12.41	−0.78	11.68	−1.51
26	12.38	12.54	+0.16	10.21	−2.17	13.84	+0.46	10.73	−1.65	7.59	−4.79
33	12.18	12.45	+0.27	11.02	−1.16	12.99	+0.81	11.19	−0.99	10.23	−1.95
47	1.71	2.11	+0.40	1.47	−0.24	1.88	+0.17	1.41	−0.30	1.25	−0.46
48	9.82	------	------	8.04	−1.78	9.47	−0.35	6.99	−2.83	6.48	−3.34
Average	------	------	+0.21	------	−0.52	------	+0.25	------	−0.49	------	−0.90

(d) That none of the methods studied indicates correctly the neutral point of ammonium citrate.

(e) That continuation of the work, including the results on a larger number of samples, will be necessary before a satisfactory basis for recommendations will be available.

(f) That the results by the citric acid and sodium citrate methods do not with present directions give promise of providing a suitable substitute for neutral ammonium citrate in the determination of reverted phosphoric acid.

If the results reported are a criterion, the adoption of either the citric

3.

results of digestion with solutions.

R. B. Deemer.)

N/10 CITRIC ACID		SODIUM CITRATE		INSOLUBLE PHOSPHORIC ACID (P_2O_5)								SAMPLE NUMBER
Phosphoric acid (P_2O_5) dissolved	Difference	Phosphoric acid (P_2O_5) dissolved	Difference	Triammonium citrate salt	Corallin	Optional	Hand	Patten	Hildebrand	N/10 citric acid	Sodium citrate	
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
5.30	−4.37	2.73	−6.94	5.63	2.87	6.23	3.60	7.09	7.40	10.00	12.57	3
3.92	−0.21	2.83	−1.32	2.32	1.92	2.56	1.80	2.45	2.64	2.53	3.62	4
4.53	−0.93	4.03	−1.43	0.79	0.70	0.99	0.87	0.84	1.13	1.72	2.22	5
6.52	−0.38	5.11	−1.79	2.14	1.94	2.34	1.82	2.20	2.44	2.52	3.93	7
5.71	−1.46	5.71	−1.46	4.14	4.10	4.34	4.15	4.25	4.39	5.60	5.60	10
5.29	−1.40	5.34	−1.35	7.32	7.29	7.51	7.18	7.24	7.41	8.72	8.67	11
3.79	−0.38	3.07	−1.10	1.17	0.96	1.40	0.89	1.16	1.53	1.55	2.27	14
3.62	−0.20	2.70	−1.12	2.05	1.65	2.13	1.47	1.94	2.09	2.25	3.17	15
3.28	−0.53	3.09	−0.72	1.16	1.15	1.10	1.24	1.22	1.08	1.69	1.88	30
3.04	−0.55	2.88	−0.71	1.72	1.79	1.76	1.72	1.82	1.79	2.27	2.43	34
6.13	−0.64	5.63	−1.14	1.21	1.21	1.24	1.16	1.26	1.25	1.85	2.35	40
3.20	−0.83	2.82	−1.21	2.06	1.98	2.13	2.05	2.00	2.17	2.89	3.27	43
5.39	−0.35	4.57	−1.17	0.02	0.10	0.19	0.18	0.02	0.10	0.37	1.19	20
6.51	−1.45	5.78	−2.18	1.32	1.35	1.39	1.33	1.21	1.30	2.77	3.50	22
4.94	−0.64	4.30	−1.28	1.55	1.50	1.54	1.37	1.64	1.48	2.19	2.83	23
5.32	−1.48	4.64	−2.16	1.64	1.94	1.72	1.62	1.77	1.87	3.12	3.80	39
5.65	−0.80	4.88	−1.57	0.14	0.23	0.25	0.20	0.21	0.19	0.94	1.71	45
18.88	−5.54	19.25	−5.17	14.19	13.87	16.28	13.75	16.03	17.19	19.73	19.36	41
6.17	−3.08	4.30	−4.95	4.91	5.02	6.38	4.75	6.10	7.58	7.99	9.86	18
8.30	−4.89	4.40	−8.79	12.51	12.43	13.60	12.04	13.29	14.02	17.40	21.30	24
7.18	−5.20	3.39	−8.99	8.89	8.73	11.06	7.43	10.54	13.68	14.09	17.88	26
7.27	−4.91	3.83	−8.35	9.94	9.67	11.10	9.13	10.93	11.88	14.85	18.29	33
2.22	+0.51	1.85	+0.14	29.53	29.13	29.77	29.36	29.83	29.99	29.02	29.39	47
8.74	−1.08	1.83	−7.99	32.07	------	33.85	32.42	34.90	35.41	33.15	40.06	48
------	−1.80	------	−3.03	------	------	------	------	------	------	------	------	

acid or sodium citrate methods studied would necessitate an entire revision of the established understanding of reverted phosphoric acid and also of the value placed on this ingredient for crop production.

The results reported, coupled with many others obtained in the course of twenty-four years' work in fertilizer inspection, tend to confirm the personal opinion of the referee that the most satisfactory solution of this problem will be to base the solvent solution not on its neutrality but on a definite amount of ammonia per liter in a solution of ammonium citrate, specific gravity 1.09, the latter determined by weight.

RECOMMENDATIONS.

It is recommended—

(1) That the study of the preparation of neutral ammonium citrate solution, its use in determining reverted phosphoric acid and possible substitutes for it in this determination be continued.

(2) That in view of the conditions resulting from the European war, whereby the price of molybdic acid has been more than quadrupled and 100 per cent molybdic acid practically removed from the market, the referee study the determination of phosphoric acid with a view to recommending an optional method not requiring the use of molybdic acid.

REPORT ON PHOSPHORIC ACID IN BASIC SLAG[1].

By C. S. LYKES[2] (Clemson Agricultural College, Clemson College, S. C.), *Associate Referee on Phosphoric Acid.*

Twelve sets of three different samples of basic slag were prepared and ten sets of samples were sent to chemists who had signified their desire to cooperate in the work.

The instructions to collaborators are substantially the same as those sent out by the referee for 1915 with the following addition under (B)[3]:

(d) In a 500 cc. volumetric flask dissolve 2 grams of the slag in about 5 cc. of nitric acid and 20 cc. of sulphuric acid, rotating the flask so that no lumps form and so that each particle will be attacked by acid. Cool and make up to mark. Determine phosphoric acid by the volumetric method, using an aliquot of 20 cc.

TABLE 1.

Moisture determinations.

ANALYST	SAMPLE	PER CENT
J. O. Clarke, Department of Agriculture, Atlanta, Ga.	1	0.47[a]
	2	0.39
	3	0.42
R. E. Pennell and C. S. Lykes, Clemson Agricultural College, Clemson College, S. C.	1	0.61
	2	0.50
	3	0.53

[a] Average of 2 determinations in all cases.

Particular attention was directed to the preparation and concentration of solutions used in the volumetric analysis.

The 500 cc. Wagner flasks must have a neck width of at least 20 mm. and must be marked at least 8 cm. below the mouth. The filtration

[1] Presented by P. F. Trowbridge.
[2] Present address, Solvay Process Company, Syracuse, N. Y.
[3] *J. Assoc. Official Agr. Chemists*, 1917, 3: 90.

must be performed immediately after rotating 30 minutes. The use is recommended of a folded No. 597, S. & S. filter paper sufficiently large to permit the whole quantity of liquid to be poured on the filter at once. If the beaker containing the mixture of phosphate and molybdate solutions is heated on the water bath to 60–70°C., a precipitate free from silicic acid results. If heating is continued for a considerably longer time, the precipitate will often be mixed with silicic acid, especially when the molybdate solution is not added to the filtrate immediately.

TABLE 2.

Determination of total phosphoric acid.

ANALYST	SAMPLE	METHOD						
		Official gravimetric, solution by I, 5 (g)[a]	Optional volumetric, solution by I, 5 (g)[a]	Official gravimetric, sulphuric and nitric acid	Volumetric, cold precipitation, sulphuric and nitric acid	Lorenz[b]	Official gravimetric, solution by I, 5 (g)[a], ferric oxid removed	Official gravimetric, solution by I, 5 (g)[a], no sodium acetate
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
J. O. Clarke	1	16.37[c]	16.50[c]	16.47[c]	16.40[c]	16.46[c]	-----	-----
	2	17.37[c]	17.20[c]	17.30[c]	17.15[c]	17.10[c]	-----	-----
	3	17.20[c]	17.22[c]	17.07[c]	17.03[c]	16.97[c]	-----	-----
R. E. Pennell and C. S. Lykes	1	16.90[d]	16.43[e]	-----	16.52[f]	-----	16.30[d]	16.72[e]
	2	17.37[e]	17.10[d]	-----	17.09[g]	-----	16.69[e]	17.13[e]
	3	17.38[d]	17.07[d]	-----	17.13[h]	-----	16.80[d]	17.13[e]

[a] *Assoc. Official Agr. Chemists, Methods*, 1916, 2.
[b] *J. Assoc. Official Agr. Chemists*, 1917, 3: 90.
[c] Average of 2 determinations.
[d] Average of 4 determinations.
[e] Average of 3 determinations.
[f] Average of 5 determinations.
[g] Average of 8 determinations.
[h] Average of 7 determinations.

TABLE 3.

Determination of available phosphoric acid.

ANALYST	SAMPLE	MOLYBDATE	METHOD		
			Optional volumetric	Lorenz	Iron citrate[a]
		per cent	*per cent*	*per cent*	*per cent*
J. O. Clarke	1	14.76[b]	14.90	14.85	14.72
	2	15.07	15.27	15.22	15.28
	3	15.42	15.57	15.58	15.40
R. E. Pennell and C. S. Lykes	1	14.82[c]	14.55[c]	14.90[d]	14.93[c]
	2	15.19[c]	14.85[c]	15.39[e]	15.25[c]
	3	15.46[c]	15.16[c]	15.78[d]	15.56[f]

[a] *J. Assoc. Official Agr. Chemists*, 1917, 3: 92.
[b] Average of 2 determinations, unless otherwise indicated.
[c] Average of 4 determinations.
[d] Average of 5 determinations.
[e] Average of 6 determinations.
[f] Average of 3 determinations.

DISCUSSION.

It will be noted that the instructions recommend the use of 5 cc. of sodium acetate solution before precipitating with magnesia mixture in the gravimetric determinations according to method **I, 5 (g)**. Reference to Table 1 shows that all results were high, averaging about 0.3 per cent above those obtained by the volumetric method. In all cases the precipitate was redissolved and the iron determined, the consequent corrected results falling about 0.3 per cent below those by the volumetric method. A perusal of the table shows a considerable variation in iron content, the samples which contained a high percentage of iron running the highest. When, however, correction for iron is made, results which are uniform, though low, are obtained.

Some difficulty was experienced in getting the slags into solution with hydrochloric and nitric acid, due to precipitation and caking of silica on the bottom of the flask, but by constant shaking this difficulty was overcome.

When samples were put into solution by method **I, 5 (g)**, all volumetric determinations were found to yield concordant results, no variation from the average by more than 0.29 per cent being noted.

On all volumetric work from nitric-sulphuric acid solutions, results from a greater number of analyses were found to agree even more closely, except on Sample 1. With samples of slag put into solution with sulphuric and nitric acid, the precipitate of phosphomolybdate was formed in larger crystals, and for this reason there was less danger of loss on filtration by running through the filter medium.

All filtering was done by suction, and a thin pad of pure white asbestos fiber was used. Due to abnormally high results obtained when filter paper or paper pulp is employed as the filter medium, the associate referee used only asbestos.

The concordant results of the several methods and the results by the iron citrate method should be noted. All methods for available phosphoric acid show very close agreement. The iron citrate method is more rapid, easier of manipulation, and results in extremely close checks.

RECOMMENDATIONS.

It is recommended—

(1) That the volumetric method from sulphuric and nitric acid solution be adopted as official for total phosphoric acid in basic slag.

(2) That the continuation of the work on the availability of phosphoric acid in basic slag be governed by the report of the field committee on this work.

REPORT ON NITROGEN.

By H. D. Haskins (Agricultural Experiment Station, Amherst, Mass.), *Referee.*

The work on nitrogen has been along the lines recommended by the referee for 1915. The work on nitrogen is presented in two reports: First, a study of the Jones and Street methods for organic nitrogen activity, which was conducted under the direction of the referee; second, a study of the ferrous-sulphate-zinc-soda method for nitrates, and the use of sodium sulphate in place of potassium sulphate in the Gunning method and its modifications, which was planned and carried out by the associate referee, Mr. R. B. Deemer.

ORGANIC NITROGEN ACTIVITY BY THE JONES AND STREET METHODS.

By reference to the proceedings of the association, it is found that the first serious consideration of organic nitrogen availability in mixed fertilizers was in 1895, when S. H. T. Hayes submitted results of a study of ten different organic nitrogenous substances. This included the use of alkaline, neutral and acid permanganate solutions, and barium hydrate solution, as well as a fractional treatment with sulphuric acid. Attention was called to the necessity of treating equal amounts of nitrogen in the permanganate digestions.

In 1896 J. P. Street gave some comparisons of organic nitrogen availability by the pepsin hydrochloric acid method and by vegetation experiments, and as a result of Street and Davidson's investigation of Hayes' method, it was recommended that the referee for 1897 be requested to investigate the permanganate methods.

In 1897 J. P. Street reported results of determinations carried out on 1 gram of material, which showed an utter lack of agreement. Certain modifications by H. B. Slade gave more promising results, and it was recommended that the method be further studied.

In 1898 R. J. Davidson submitted results obtained by the pepsin hydrochloric acid and the permanganate methods. C. H. Jones for the first time presented his modifications, which consisted of the use of 100 cc. of a solution made up by using 16 grams of potassium permanganate and 150 grams of sodium hydroxid per liter, employing enough sample to furnish 45 mg. of nitrogen, digesting, below boiling, for 1 hour and allowing 1 hour for distillation. He also submitted his interpretation of results by this method, classing the materials as either good or questionable, according to whether they ran over or under 50 per cent in nitrogen activity.

In 1899 F. S. Shiver concluded that the neutral gave more promising

results than the alkaline permanganate method and recommended a further study of the neutral method. At this time the Jones method employed 45 mg. and the Street method 75 mg. of nitrogen.

In 1900 W. R. Perkins called attention to the necessity of washing the fertilizer with water to remove soluble phosphates, etc., before treatment with the permanganate solution. Although results of the year's work were discouraging, he recommended that both of the permanganate methods be further studied.

In 1901 W. R. Perkins studied the two methods and reported results which were not entirely satisfactory, but with some misgivings he recommended that the neutral method be adopted as provisional, and that further study be given the alkaline, or Jones, method.

In 1902 F. W. Morse concluded that the alkaline permanganate method was worthy of further investigation, and recommended that both methods be further studied with a view to getting more concordant results. In 1903 F. W. Morse continued the study of the two methods, recommending some modifications of the neutral method, and also further study of both the neutral and the alkaline methods.

In 1904 C. H. Jones sent out three samples of fertilizer and received reports of results from 15 chemists. Certain improvements and modifications were made in the alkaline method, and it was recommended that this method be adopted by the association as provisional.

In 1905 no cooperative work was done on these methods and no report was made to the association.

In 1906 J. H. Gibboney studied the two methods with two mixed fertilizers of known make-up, and received the cooperation of fifteen chemists. He stated that, although the alkaline method gives low results, it presents greater possibilities than the neutral procedure, and recommended that both be studied further.

In 1907, 1908 and 1909 no work was done on either method.

In 1910 C. H. Jones revived the interest of the association in the two methods. In the case of the neutral method, the important changes since its adoption as provisional were the employment of an equivalent of 45 mg. of water insoluble organic nitrogen for the determination, and the elimination of the filter paper during the permanganate digestion. The alkaline method had been modified by the use of material equivalent to 50 mg. of water-insoluble organic nitrogen. With mixed goods an increase in the strength of permanganate solution from 1.6 to 2.5 per cent was effected. The data furnished showed a very satisfactory agreement between the two revised methods and carefully conducted pot experiments by Messrs. Hartwell and Pemberton on twelve complete fertilizers.

In 1911 no additional work was done on the two methods.

In 1912 C. L. Hare studied the two methods by the use of four fertilizer samples, seven analysts taking part in the work. The neutral permanganate method gave fairly uniform results in the hands of different analysts, but the alkaline permanganate methods gave satisfactory results only with base goods and mixed fertilizers.

In 1913 C. L. Hare was of the opinion that the methods furnished a fair basis for arriving at the relative activity of the organic nitrogen in various fertilizers, and that either method would serve to differentiate the good forms of nitrogen from the bad, but expressed the belief that the small number of results secured by the association would hardly warrant a positive recommendation that the methods be adopted as official.

In 1914 R. N. Brackett reported that the Jones (alkaline) method gave results more in accordance with pot tests than the Street (neutral) method, and that, while the Jones method was shorter, the Street method in the hands of inexperienced workers gave more uniform results. He recommended that both methods be studied in order to increase the accuracy of the determination of the water-insoluble organic nitrogen and to overcome the difficulties of distillation, and further that they be adopted as official.

In 1915 R. N. Brackett reported results which made it evident that the two methods in the hands of analysts who were familiar with the manipulation involved and who had equipment suitable for the work served to differentiate the good from the bad nitrogen.

Three samples of mixed fertilizer were used in the study of the two methods by your present referee. The make-up of the fertilizers was as follows:

Sample 1.

Weight of cottonseed meal	50 per cent
Weight of 16 per cent acid phosphate	25 per cent
Weight of high grade red dried blood	25 per cent

Sample 2.

Weight of ground garbage tankage, degreased	50 per cent
Weight of 16 per cent acid phosphate	25 per cent
Weight of cottonseed meal	25 per cent

Sample 3.

Weight of high grade red dried blood	25 per cent
Weight of 16 per cent acid phosphate	50 per cent
Weight of concentrated tankage	25 per cent

A set of these samples with the following instructions was sent to the collaborators:

You are requested to analyze each sample for total nitrogen according to the official Gunning method, the water-insoluble organic nitrogen and the available nitrogen according to the two methods enclosed herewith. Each sample should also be analyzed for its moisture content.

In the case of the Street method report results as follows—total nitrogen, ammoniacal nitrogen, water-insoluble organic nitrogen, permanganate-insoluble nitrogen; in the case of the Jones method—total nitrogen, ammoniacal nitrogen, water-insoluble organic nitrogen, nitrogen liberated by the alkaline permanganate solution.

ALKALINE PERMANGANATE METHOD FOR ORGANIC NITROGEN ACTIVITY.

(a) Transfer an amount of material equivalent to 50 mg. of water-insoluble organic nitrogen[1] to an 11 cm. No. 597, S. & S. filter paper as a preliminary to washing with water. In case of Samples 1 and 2, wash with 40 cc. of ether on dry filter paper, using 10 cc. with each washing. Wash once with alcohol to displace ether, and wash with successive portions of water at room temperature until the filtrate amounts to about 250 cc.

(b) Transfer the residue, with 20 cc. of water, by means of a 20 cc. pipette drawn out to a fine point, so that complete delivery takes about 25 seconds, the filter paper being opened and laid in an elliptical shaped piece of tin bent so that the washings will be properly conducted into the mouth of the flask, to a 500–600 cc. Kjeldahl distillation flask (round-bottomed preferred, but if flat-bottomed is used, incline at an angle of 30°). Add 15–20 small glass beads or fragments of pumice stone to prevent bumping, and 100 cc. of alkaline permanganate solution (25 grams of pure potassium permanganate and 150 grams of sodium hydroxid, separately dissolved in water, the solution cooled, mixed and made to volume of 1 liter). A piece of paraffin about the size of a small pea may be added if danger from frothing is apparent. Connect with an upright condenser to which a receiver containing standard acid has been attached. It is recommended that the distillate be collected in a 100 cc. graduated open cylinder. Digest slowly, below distillation point, with very low flame, using coarse wire gauze and asbestos paper between flask and flame, for at least 30 minutes. Gradually raise the temperature and when danger (if any) from frothing has ceased, distil until 95 cc. of distillate are obtained and titrate as usual. In cases where a tendency to froth is noticed, lengthen the digestion period and no trouble will be experienced when the distillation is begun. During the digestion, gently rotate the flask occasionally, particularly if the material shows a tendency to adhere to the sides. It is recommended that as nearly as possible 90 minutes be taken for the digestion and distillation. The nitrogen thus obtained is the active water-insoluble organic nitrogen.

MODIFIED NEUTRAL PERMANGANATE METHOD FOR THE AVAILABILITY OF ORGANIC NITROGEN.

Weigh a quantity of the fertilizer equivalent to 50 mg. of water insoluble organic nitrogen[1] on a moistened 11 cm. No. 597, S. & S. filter paper, and wash with successive portions of water at room temperature until the filtrates amount to 250 cc. Transfer

[1] Determined by extracting 1 gram of the material on an 11 cm. No. 597, S. & S. filter paper with water at room temperature, until the filtrate amounts to about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper, if necessary.

TABLE 1.

Availability of the organic nitrogen of Sample 1.

ANALYST	MOISTURE	TOTAL NITROGEN	AMMONIA NITROGEN	WATER-INSOLUBLE ORGANIC NITROGEN	JONES		STREET	
					Nitrogen liberated by alkaline permanganate	Active water-insoluble organic nitrogen	Permanganate-insoluble organic nitrogen	Active water-insoluble organic nitrogen
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
E. F. Berger, Agricultural Experiment Station, E. Lansing, Mich.	----	6.71	0.06	6.52	4.35	67.0	0.43	93.0
E. A. DeWindt, Agricultural Experiment Station, E. Lansing, Mich.	8.35	----	----	6.58	4.30	65.0	0.50	92.0
C. H. Jones, Agricultural Experiment Station, Burlington, Vt.	6.72	6.52	0.07	6.20	4.09	66.0	0.43	93.0
L. S. Walker, Agricultural Experiment Station, Amherst, Mass.	7.28	7.07	----	6.41	3.91	61.0	0.18	97.0
R. B. Deemer, State Chemist Department, La Fayette, Ind.	5.53	6.68	0.07	6.28	4.70	75.0	0.32	95.0
R. E. Ingham, Virginia-Carolina Chemical Co., Richmond, Va.	6.01	6.85	0.05	6.51	4.67	72.0	0.55	91.0
F. N. Smalley, Southern Cotton Oil Co., Savannah, Ga.	6.32	6.83	0.04	6.40	3.85	60.0	0.20	97.0
C. A. Jacobson, Agricultural Experiment Station, Reno, Nev.	----	----	----	6.47	4.76	74.0	[a]	[a]
Swift & Company								
Analyst "A"	6.69	7.13	----	6.81	4.71	69.0	0.47	93.0
Analyst "B"	----	7.16	----	6.76	4.76	70.0	0.55	92.0
H. S. Chilton and I. D. Sessums, Agricultural and Mechanical College, Agricultural College, Miss.	6.97	7.08	----	6.57	3.32	51.0	0.73	89.0
J. H. Perry, Agricultural Experiment Station, Orono, Me.	5.30	6.72	0.07	6.32	3.25	51.0	0.29	95.0
L. W. Bradley, Department of Agriculture, Atlanta, Ga.	5.97	6.85	0.06	6.40	----	----	----	----
Average	6.51	6.87	0.06	6.48	4.22	65.1	0.42	93.4

[a] Unable to interpret results.

the insoluble residue with 25 cc. of tepid water (the bulk of the residue may be removed by a small spatula, care being taken not to scrape or rough up the paper, which may be laid on a piece of tin bent in the form of an ellipse; a 25 cc. pipette that will deliver its volume of water in about 25 seconds will be found satisfactory) to a 300 cc. low-form Griffin beaker, add 1 gram of dry sodium carbonate and 100 cc. of 2% permanganate solution. Digest in a steam or hot water bath for 30 minutes at the temperature of boiling water, covering the beaker with a watch glass and setting well down into the bath so that the level of the liquid in the beaker is below that of the bath. Stir twice at intervals of 10 minutes. At the end of the digestion remove from the bath, add 100 cc. of cold water and filter through a heavy 15 or 18.5 cm. folded filter. Wash small quantities at a time with cold water until the total filtrate amounts to about 400 cc. Determine nitrogen in the residue and filter, correcting for the nitrogen of the filter.

Results have been received from eleven different sources, including thirteen different analysts. Very little or no comment was made by any of the collaborators.

TABLE 2.

Availability of the organic nitrogen of Sample 2.

ANALYST	MOISTURE	TOTAL NITROGEN	AMMONIA NITROGEN	WATER-INSOLUBLE ORGANIC NITROGEN	JONES		STREET	
					Nitrogen liberated by alkaline permanganate	Active water-insoluble organic nitrogen	Permanganate-insoluble organic nitrogen	Active water-insoluble organic nitrogen
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
E. F. Berger	----	2.90	0.05	2.55	1.03	40.0	0.36	86.0
E. A. DeWindt	7.09	----	----	2.68	0.98	37.0	0.57	79.0
C. H. Jones	5.60	2.84	0.04	2.60	1.04	40.0	0.30	88.0
L. S. Walker	5.60	3.15	----	2.54	0.96	38.0	0.23	90.0
R. B. Deemer	4.42	2.93	0.11	2.60	1.10	42.0	0.43	83.0
R. E. Ingham	4.80	2.98	0.05	2.65	1.29	49.0	0.52	81.0
F. N. Smalley	5.30	2.89	0.07	2.53	[a]	[a]	0.55	78.0
C. A. Jacobson	----	----	----	2.58	0.89	34.0	[a]	[a]
Swift & Company								
Analyst "A"	5.35	3.18	----	2.87	1.30	45.0	0.39	86.0
Analyst "B"	----	3.21	----	2.88	1.31	45.0	0.41	86.0
H. S. Chilton and I. D. Sessums	5.38	3.06	----	2.48	0.84	34.0	0.44	82.0
J. H. Perry	5.98	3.04	0.10	2.68	0.77	29.0	0.26	90.0
L. W. Bradley	4.90	3.02	0.05	2.63	0.87	33.0	0.60	77.0
Average	5.44	3.02	0.07	2.64	1.03	38.8	0.42	83.8

[a] Unable to interpret results.

TABLE 3.

Availability of the organic nitrogen of Sample 3.

ANALYST	MOISTURE	TOTAL NITROGEN	AMMONIA NITROGEN	WATER-INSOLUBLE ORGANIC NITROGEN	JONES		STREET	
					Nitrogen liberated by alkaline permanganate	Active water-insoluble organic nitrogen	Permanganate-insoluble organic nitrogen	Active water-insoluble organic nitrogen
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cen*
E. F. Berger	----	6.19	0.19	3.91	3.07	79.0	0.22	94.0
E. A. DeWindt	8.20	----	----	3.91	2.82	72.0	0.16	96.0
C. H. Jones	6.52	6.07	0.14	3.73	2.72	73.0	0.27	93.0
L. S. Walker	6.42	6.70	----	3.89	2.67	69.0	0.14	96.0
R. B. Deemer	5.10	6.28	0.23	3.77	3.04	81.0	0.16	96.0
R. E. Ingham	5.29	6.34	0.16	3.99	3.02	76.0	0.32	92.0
F. N. Smalley	5.50	6.31	0.20	3.72	[a]	[a]	0.14	96.0
C. A. Jacobson	----	----	----	3.92	2.93	75.0	[a]	[a]
Swift & Company								
Analyst "A"	6.50	6.69	----	4.09	3.05	75.0	0.21	95.0
Analyst "B"	----	6.63	----	4.08	3.01	74.0	0.22	95.0
H. S. Chilton and I. D. Sessums	6.00	6.59	----	3.77	2.29	61.0	0.54	86.0
J. H. Perry	6.70	6.35	0.19	4.07	2.66	65.0	0.15	96.0
L. W. Bradley	5.60	6.42	0.17	3.99	2.14	54.0	1.07	73.0
Average	6.18	6.41	0.18	3.91	2.78	71.2	0.30	92.3

[a] Unable to interpret results.

Without any attempt to explain the rather wide variation which exists in the total nitrogen and moisture determinations of Sample 1, it may be said that, with two or three exceptions, the total water-insoluble nitrogen and the active water-insoluble nitrogen results by both the methods are reasonably satisfactory. If 50 per cent for the alkaline and 85 per cent for the neutral method be allowed as the lowest figures that would indicate a passing quality of organic nitrogen, on the basis of 50 mg. of water-insoluble nitrogen, both of the methods would class the nitrogen in this sample as good.

In the case of Sample 2, although the total and water-insoluble nitrogen may be in as close agreement as in Sample 1, the results by the two methods are not so pleasing. The alkaline method condemns the nitrogen in all cases, the percentage of activities shown varying from 29 to

49, with an average of 39 per cent. In the case of the neutral method, six of the determinations would condemn, four might class the nitrogen as suspicious, and two would pass the nitrogen as being derived from a satisfactory source. It would seem that in this particular case, 85 per cent was rather too low an arbitrary figure to indicate nitrogen of passing quality. Apparently this is recognized by the author of the method, Mr. J. P. Street, for he says, "I should view with considerable suspicion one falling appreciably below 90 per cent". Two analysts obtained barely 90 per cent activity; the others were from 2 to 13 points below this figure on this particular sample.

On Sample 3 both methods gave satisfactory results, with the exception of two determinations by the neutral method.

TABLE 4.

Comparative tests of nitrogen availability[a].

MATERIAL	NITROGEN ACTIVITY BY ALKALINE PERMANGANATE METHOD	NITROGEN ACTIVITY BY DUPLICATE VEGETATION TESTS (OATS) 0.42 GRAM NITROGEN
	per cent	*per cent*
Dried blood (unwashed)	--	80
Sheep manure	29	toxic
Ground tobacco stems	18	toxic
Dried blood (water-insoluble nitrogen)	76	75
Castor pomace	53	70
Complete fertilizer No. 1	36	19[b]
Complete fertilizer No. 2	46	18
Complete fertilizer No. 3	48	24
Complete fertilizer No. 4	53	39
Complete fertilizer No. 5	41	31
Complete fertilizer No. 6	51	32
Complete fertilizer No. 7	58	70
Complete fertilizer No. 8	49	46
Complete fertilizer No. 9	37	37
Complete fertilizer No. 10	54	49
Complete fertilizer No. 11	57	68
Complete fertilizer No. 12	46	40
Complete fertilizer No. 13	45	15
Complete fertilizer No. 14	48	18
Complete fertilizer No. 15	48	33
Complete fertilizer No. 16	46	25
Complete fertilizer No. 17	60	63
Complete fertilizer No. 18	47	48
Complete fertilizer No. 19	75	70
Complete fertilizer No. 20	49	40

[a] Mass. Agr. Expt. Sta., Control Ser., Bull. 2: 30.
[b] Certain observed facts indicate that this figure is perhaps too low.

The referee regrets that a lack of time prevented the carrying on of vegetation tests with these three fertilizers. During the past two years, however, the referee has conducted comparative tests which give the relative nitrogen activity by the laboratory methods, as compared with vegetation tests, on the basis of water-insoluble organic nitrogen[1].

Some tabulated results are submitted taken from these two publications. It will be seen that the neutral method was not included in Table 4, while Table 5 includes both laboratory methods. Many of the samples studied during the two years were selected on account of the suspicious character of their nitrogen, although other brands were included which were known to contain only nitrogen of good quality.

In the case of the vegetation tests the increase in yield of dry matter over the no-nitrogen pots obtained with *unwashed* dried blood is placed at 80 per cent, and the increases in yield of dry matter due to the other nitrogen sources (derived from the water-insoluble portion of the various fertilizers) are compared with it.

A study of Table 4 suggests the following conclusions:

(1) In the case of the sheep manure and ground tobacco stems the large amount of organic matter necessary to furnish 0.42 gram of water-insoluble organic nitrogen seemed to have some injurious effect. A much lower yield of dry matter, accompanied by a much reduced root growth, was obtained than on the no-nitrogen pots.

(2) All of the brands of complete fertilizer showing a questionable nitrogen activity by the alkaline permanganate method gave a relatively low nitrogen activity by the vegetation experiment, the average of sixteen such cases being 46.5 per cent by the alkaline permanganate method, and 32 per cent by the vegetation experiment. It should be noted in this connection that the laboratory method gives full credit in almost every instance.

(3) Sample 11 was the only complete fertilizer tested which shows the water-insoluble organic nitrogen to be of good quality when measured by the vegetation experiment, and of suspicious quality by the laboratory method. A large proportion of the organic nitrogen in this brand was derived from cottonseed meal and castor pomace. The results obtained with castor pomace also show that the laboratory method is likely to give results, somewhat too low, on this class of organic ammoniates. This bears out the observations of C. H. Jones of Vermont and B. L. Hartwell of Rhode Island.

(4) Allowing 50 per cent as indicating a passing quality of organic nitrogen by the alkaline method, we find that only three out of twenty-five cases (Nos. 10, 6 and 4), which showed nitrogen of poor quality by vegetation experiment, would have failed detection by the alkaline method.

[1] Mass. Agr. Expt. Sta., Control Ser., Bull. **2**: 28; **4**: 32.

TABLE 5.

Comparative tests of nitrogen availability[a].

POT NUMBER	WATER-INSOLUBLE NITROGEN PER POT[b]	INCREASE OF NITROGEN RECOVERED OVER NO-NITROGEN POTS	RELATIVE NITROGEN ACTIVITY[c]	COMPARATIVE NITROGEN ACTIVITIES	
				Alkaline permanganate method	Neutral permanganate method
	gram	*gram*	*per cent*	*per cent*	*per cent*
1 A, B, C, D, E, F, G, H (blood)	0.42	0.141	80.00	80.00	----
5 A, B, C, D (nitrate of soda)	0.42	0.146	82.84	----	----
15 A, B (castor pomace)	0.42	0.101	57.31	60.19	----
60 A, B (cottonseed meal)	0.42	0.121	68.65	50.20	95.70
59 A, B (dried blood, washed)	0.42	0.153	86.80	71.00	----
62 A, B (garbage tankage)	0.42	0.041	23.26	44.81	----
6 A, B	0.42	0.029	16.45	48.00	79.30
8 A, B	0.42	0.061	34.61	46.40	82.90
10 A, B	0.42	0.015	8.51	44.00	56.00
11 A, B	0.42	No increase	----	34.00	43.75
12 A, B	0.42	0.105	59.57	54.20	93.40
14 A, B	0.42	0.065	36.88	55.80	82.00
16 A, B	0.42	0.069	39.15	42.40	76.75
17 A, B	0.42	0.061	34.61	54.80	85.00
19 A, B	0.42	0.089	50.50	61.00	94.00
21 A, B	0.42	0.036	20.43	43.60	----
22 A, B	0.42	0.069	39.15	48.20	80.00
23 A, B	0.42	0.082	46.52	47.20	85.00
25 A, B	0.42	No increase	----	37.20	70.00
26 A, B	0.42	0.029	16.45	38.20	62.00
28 A, B	0.42	0.055	31.21	40.80	78.00
29 A, B	0.42	0.089	50.50	47.80	91.00
31 A, B	0.42	0.098	55.60	52.00	87.00
32 A, B	0.42	0.123	69.80	66.00	87.00
34 A, B	0.42	0.019	10.78	47.20	59.00
36 A, B	0.42	0.092	52.20	56.00	89.00
37 A, B	0.42	0.090	51.06	52.00	88.00
38 A, B	0.42	0.096	54.47	58.00	95.00
39 A, B	0.42	0.132	74.89	60.00	95.00
41 A, B	0.42	0.120	68.09	63.00	88.00
42 A, B	0.42	0.073	41.42	35.60	91.00
44 A, B	0.42	0.101	57.30	39.00	91.00
45 A, B	0.42	0.110	62.41	39.00	87.00
47 A, B	0.42	0.094	53.33	50.00	84.00
48 A, B	0.42	0.097	55.04	56.00	86.00
49 A, B	0.42	0.125	70.92	62.00	95.00
51 A, B	0.42	0.037	20.99	26.00	73.00
52 A, B	0.42	0.005	2.84	24.00	67.00
54 A, B	0.42	0.024	13.62	44.00	79.00
55 A, B	0.42	0.007	3.97	41.00	50.00
56 A, B	0.42	0.105	59.57	49.00	89.00
58 A, B	0.42	0.083	47.09	37.00	93.00

[a] Mass. Agr. Expt. Sta., Control Ser., Bull. 4: 36, with the exception of data in last column.
[b] Dried blood (pots 1 A, B, C, D, E, F, G, H), castor pomace (pots 15 A, B), garbage tankage (pots 62 A, B), received their nitrogen as indicated from unwashed material.
[c] Basis: Nitrogen recovered, dried blood at 80 per cent.

A study of Table 5 shows that in twenty-five out of forty-one cases (61 per cent) the alkaline permanganate method indicates higher nitrogen activities than does the vegetation test; that in four out of forty-one cases (9.75 per cent) the alkaline permanganate method fails to differentiate between the low and high grade forms of organic ammoniates. In three of these cases the fertilizers were known to contain organic vegetable ammoniates (castor pomace and cottonseed meal). It would appear that the chief criticism of the method is that it sometimes gives too low results with organic *vegetable* ammoniates of good quality.

In case of the neutral method, allowing 85 per cent as indicating a passing quality of the organic nitrogen, it is found that out of a total of twenty-one samples containing nitrogen of low grade character, four cases would have failed detection by the neutral method.

All the pot work which has been done in the study of these two methods shows that the alkaline gives nitrogen availabilities more closely agreeing with actual vegetation tests.

In Table 5 it is found that out of thirty-six tests made, the average nitrogen activity by the vegetation test was 43.07 per cent, by the alkaline method 48.94 per cent, and by the neutral method 81.33 per cent. The results given herewith seem to be in harmony with results obtained at the Rhode Island and Vermont Agricultural Experiment Stations. It seems to the referee that there can be no doubt among the members of the association, who possess properly equipped laboratories for the work and who have given these two methods, as modified and improved to date, a fair trial that both the alkaline and neutral permanganate tests are reliable in differentiating between the good and the poor forms of organic nitrogen. It is the opinion of the referee that efficiency with either method is very largely a question of proper equipment, experience and familiarity with the work, and he does not feel justified in recommending further study by the association. He does feel that both methods should be used in control work, particularly on fertilizers containing nitrogen of suspicious quality.

REPORT ON NITROGEN DETERMINATION.

By R. B. Deemer[1] (State Chemist Department, La Fayette, Ind.),
Associate Referee.

The work was confined to a study of the ferrous sulphate-zinc-soda method for the determination of nitrogen in sodium nitrate. The material used was commercial sodium nitrate, ground to pass a 30-mesh sieve.

[1] Present address, Bureau of Plant Industry, Washington, D. C.

INSTRUCTIONS FOR TOTAL NITROGEN DETERMINATION.

PREPARATION OF SAMPLE.

Pour out the sample and carefully mix, finally spreading thinly and uniformly over glazed paper. In weighing out remove small portions, with point of the spatula, from various parts of the sample thus spread out.

MOISTURE.

Heat 2 grams of the sample at 125–130°C. to constant weight.

NITROGEN.

Determine nitrogen by the following methods:

Kjeldahl Method Modified.

Place 0.5 gram of the sample in a digestion flask, add 30 cc. of sulphuric acid containing 2 grams of salicylic acid, allow to stand at least 30 minutes (overnight if time permits) and then add gradually 2 grams of zinc dust, thoroughly shaking the contents of the flask. Digest over a low flame until frothing ceases, then raise the heat to brisk boiling, continue boiling for 10 minutes or until white fumes no longer escape from the neck of the flask. Add 0.7 gram of mercuric oxid and boil briskly for 3 hours; add 10 cc. more of sulphuric acid as required to maintain the volume above 20 cc. during the digestion. Oxidize with potassium permanganate and complete the distillation as usual.

Report time of treatment with salicylic acid mixture.

Make determinations in blank on all reagents with above method using 2 grams of sugar; report as cc. of N/2 acid.

Ferrous Sulphate-Zinc-Soda Method.

(a) Place 0.5 gram of the sample in a 600–700 cc. flask, add 200 cc. of water, 5 grams of powdered zinc, 1–2 grams of crystallized ferrous sulphate and 50 cc. of sodium hydroxid solution (36° Baumé). Distil, collect in the usual way in N/10 sulphuric acid and titrate.

(b) Repeat (a) placing a plug of glass wool in the neck of the flask before connecting with the distillation apparatus.

(c) Weigh out 5 grams of the sample, dissolve in 250 cc. flask, make to volume, pipette out 25 cc. aliquots and proceed as in (a) and (b).

(d) In case it is desired to use a small amount of paraffin to prevent frothing, make determinations in addition to (a), (b), and (c), marking them (f), (g), and (h).

(e) Repeat (a) without sample and report blank, if any, as cc. N/2 acid.

COMMENTS OF COLLABORATORS.

W. D. Richardson.—It was our experience in the Kjeldahl modified method to obtain low results. By the ferrous sulphate-zinc-soda method, (a) and (c), we were unable to get satisfactory results. We had trouble with iron coming over in the distillate. Similarly where glass wool was used, (b) and (c), in the neck of the flask, we obtained quite satisfactory results. We do not use connecting bulbs in our distillation apparatus, which may account for some of the trouble experienced.

TABLE 1.

Nitrogen in nitrate of soda.

ANALYST	KJELDAHL MODIFIED	FERROUS SULPHATE-ZINC-SODA			
		0.5 gram no wool	0.5 gram and wool	5 grams to 250 cc. −25 cc. no wool	5 grams to 250 cc. −25 cc. and wool
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
H. S. Chilton, Agricultural College, Agricultural College, Miss.	15.58[a]	16.55[a]	16.07	16.16	----
Swift & Company, Chemical Laboratory, Chicago, Ill.					
Analyst "A"	15.51[a]	----	16.39[a]	----	16.56[a]
Analyst "B"	15.63[a]	----	16.33[a]	----	16.36[a]
V. B. Hausknecht, Department of Agriculture, Harrisburg, Pa.	15.65[a]	16.57[a]	16.02	16.50[a]	16.40[a]
R. I. Ingham, Virginia-Carolina Chemical Co., Richmond, Va.	15.85	15.98	15.80	15.89	15.83
J. M. Bartlett, Agricultural Experiment Station, Orono, Me.	16.18	16.24	----	16.27	16.20
H. C. Moore, Armour Fertilizer Works, Atlanta, Ga.	16.15	15.86	16.12	16.01	----
C. H. Jones, Agricultural Experiment Station, Burlington, Vt.	15.96	15.72	15.72	16.06	15.72
L. B. Johnson, Department of Agriculture, Raleigh, N. C.	15.69	15.74	15.75	15.69	15.81
L. W. Bradley, Department of Agriculture, Atlanta, Ga.	15.88	15.90	15.94	15.83	15.84
E. F. Berger, Agricultural Experiment Station, Lansing, Mich.	15.52[a]	15.76	15.74	15.76	----
E. A. Dewindt, Agricultural Experiment Station, Lansing, Mich.	15.63	15.78	15.75	15.72	----
Armour & Company, Chemical Laboratory, Chicago, Ill.					
R. A. Green	----	16.03	16.04	16.03	16.05
O. E. Meeker	----	16.06	16.05	16.08	16.10
L. S. Fry	----	16.04	----	16.05	----
L. S. Walker, Agricultural Experiment Station, Amherst, Mass.	16.19	----	----	15.57[a]	15.59[a]
R. B. Deemer, State Chemist Department, La Fayette, Ind.	15.96	15.57[a]	15.53[a]	15.75[a]	15.52[a]
Averages	15.94	15.92	15.99	15.94	15.94

[a] Omitted from average.

TABLE 2.

Nitrogen determinations by miscellaneous methods.

ANALYST	METHOD	NITROGEN
		per cent
W. D. Richardson, Swift & Company, Chicago, Ill.		
V. B. Hausknecht, Department of Agriculture, Harrisburg, Pa.	Ulsch-Street	15.94
R. E. Ingham, Virginia-Carolina Chemical Co., Richmond, Va.	Gunning modified	15.87
C. H. Jones, Agricultural Experiment Station, Burlington, Vt.		
H. C. Moore, Armour Fertilizer Works, Atlanta, Ga.	Kjeldahl-Gunning modified	16.18
R. B. Deemer, State Chemist Department, La Fayette, Ind.	Zinc-iron	15.82
L. S. Walker, Agricultural Experiment Station, Amherst, Mass.	Zinc-iron	15.98
Armour & Company, Chemical Laboratory, Chicago, Ill.		
R. A. Green	Kjeldahl-Gunning modified	15.74
O. E. Meeker		15.71
L. S. Fry		15.72
L. W. Bradley, Department of Agriculture, Atlanta, Ga.	Gunning modified	16.00

F. B. Carpenter.—It has been our experience, when making nitrogen determinations by the ferrous sulphate method, that if the apparatus is connected up with a plain bulb tube and no glass wool is used the results are invariably high. In this case we used an ordinary trap bulb, and even with this the tendency is higher without glass wool.

J. M. Bartlett.—The ferrous sulphate-zinc-soda method seems to be a rapid, accurate and desirable method for this material. I used a 750 cc. flask tipped at an angle of 45° for the distillation and had no trouble with frothing.

H. C. Moore.—We had some trouble with the ferrous sulphate-zinc-soda method on account of the sample frothing over. The distillation was finally made at a very low temperature.

Paul Rudnick.—The ferrous sulphate-zinc-soda method not only gives consistently uniform results, but works very smoothly and easily.

H. D. Haskins.—A number of tests were lost by frothing in cases where glass wool was not used. I believe it is a precaution that is quite necessary.

RELIABILITY OF THE METHOD.

A comparison of the results (Table 1) obtained by the method under study with those obtained by the Kjeldahl modified and other methods (Table 2) shows that reliable results are obtained.

TABLE 3.

Substitution of sodium sulphate for potassium sulphate.

(Nitrogen as per cent.)

FERTILIZERS				FEEDS		
		GUNNING MODIFIED			GUNNING	
SAMPLE NUMBER	KJELDAHL MODIFIED	Potassium sulphate	Sodium sulphate	SAMPLE NUMBER	Potassium sulphate plus 0.2 gram copper sulphate	Sodium sulphate plus 0.2 gram copper sulphate
1	1.68	1.72	1.73	26	2.28	2.17
2	1.75	1.68	1.69	27	2.89	2.86
3	0.84	0.85	0.88	28	1.47	1.47
4	0.64	0.63	0.64	29	2.59	2.55
5	1.07	1.09	1.08	30	1.61	1.61
6	1.21	1.14	1.17	31	1.47	1.47
7	1.68	1.58	1.65	32	1.50	1.44
8	1.77	1.72	1.74	33	2.48	2.49
9	0.93	0.88	0.87	34	2.48	2.45
10	0.50	0.46	0.46	35	2.40	2.45
11	1.77	1.79	1.78	36	3.79	3.72
12	0.75	0.67	0.69	37	2.78	2.76
13	1.24	1.23	1.28	38	1.64	1.68
14	1.30	1.25	1.28	39	2.45	2.44
15	0.95	0.89	0.90	40	1.47	1.59
16	1.28	1.28	1.28	41	1.24	1.26
17	1.20	1.20	1.21	42	2.70	2.67
18	1.12	1.11	1.09	43	1.46	1.40
19	1.51	1.49	1.49	44	6.84	6.88
20	----	1.23	1.24	45	6.35	6.43
21	0.53	0.53	0.49	46	2.55	2.60
22	1.14	1.12	1.14	47	2.70	2.79
23	0.47	0.51	0.51			
24	0.89	0.89	0.90			
25	1.72	1.76	1.80			

LOSS OF NITROGEN.

It is the opinion of the referee, Mr. Haskins, that loss of nitrogen may occur in the Kjeldahl modified method when used upon nitrate of soda if the oxidation is completed with permanganate in the usual way. Mr. L. S. Walker, of his laboratory, reports 16.19% (2 determinations) without the use of permanganate. Using permanganate I obtained 15.96% (3 determinations); and 16.00% (3 determinations) when no permanganate was used.

SUBSTITUTION OF SODIUM SULPHATE FOR POTASSIUM SULPHATE.

A brief study was made of the use of sodium sulphate in place of potassium sulphate in the Gunning method and its modifications. An average of 25 samples of fertilizers with the Kjeldahl modified gave 1.17% nitrogen; with the Gunning modified and potassium sulphate 1.11%; and with sodium sulphate 1.16% nitrogen (Table 3). The average

of 22 feed samples gave with the Gunning method and potassium sulphate 2.77% and with sodium sulphate 2.60% of nitrogen. When sodium sulphate is used some trouble is experienced with caking upon cooling after the digestion; but if the molecular equivalent of potassium sulphate is used, and care taken to dilute as soon as sufficiently cooled, this does not cause great inconvenience.

RECOMMENDATIONS.

It is recommended—

(1) That the tentative ferrous sulphate-zinc-soda method be adopted as official. Owing to the conflicting results of previous work it is suggested that the use of glass wool in the neck of the distillation flask receive further study.

(2) That further study be made of the effect of permanganate at the end of the digestion in the Kjeldahl modified method when used on nitrate of soda.

(3) That the use of sodium sulphate in the Gunning method in place of potassium sulphate be tried out on a variety of organic substances of known origin and of difficult oxidation.

SUBSTITUTION OF SODIUM SULPHATE FOR POTASSIUM SULPHATE IN THE KJELDAHL-GUNNING-ARNOLD METHOD FOR THE DETERMINATION OF AMMONIA IN FERTILIZERS.

By T. D. JARRELL[1] (State College of Agriculture, College Park, Md.).

In view of the present high price of potassium sulphate and the comparative low price of sodium sulphate, tests were made of the use of the latter in the Kjeldahl-Gunning-Arnold method for the determination of ammonia in fertilizers.

Latshaw[2] reports results on ten different samples, substituting sodium sulphate for potassium sulphate, using the Gunning copper method. These results show a very close agreement between the two processes and he concludes that sodium sulphate can be used as well as potassium sulphate as a catalytic agent for raising the boiling point of sulphuric acid in any kind of material. Latshaw discusses the comparative costs of these salts at their present prices and the saving realized when substituting sodium sulphate, so it is unnecessary to discuss this phase in this paper.

Nine samples were used, namely: Dissolved hair waste; dissolved leather waste; dried blood; fish scraps; cottonseed meal; tankage; raw bone; 2 to 9 base goods; and calcium cyanamid. The following table shows the results obtained:

---

[1] Present address, Bureau of Chemistry, Washington, D. C.
[2] *J. Ind. Eng. Chem.*, 1916, 8: 586.

Comparison of sodium sulphate with potassium sulphate.

SAMPLE	AMMONIA FOUND USING	
	Potassium sulphate	Sodium sulphate
	per cent	*per cent*
No. 1. Hair waste	11.44	11.44
	11.34	11.36
	11.36	11.40
Average	11.38	11.40
No. 2. Leather waste	9.48	9.48
	9.46	9.48
	9.58	9.52
Average	9.51	9.49
No. 3. Dried blood	15.76	15.70
	15.66	15.76
	15.76	15.62
Average	15.73	15.69
No. 4. Fish scraps	8.88	8.80
	8.80	8.84
Average	8.84	8.82
No. 5. Cottonseed meal	6.62	6.62
	6.58	6.66
Average	6.60	6.64
No. 6. Tankage	9.08	9.18
	9.08	9.07
Average	9.08	9.13
No. 7. Raw bone	4.47	4.54
	4.45	4.35
	4.52	4.47
Average	4.48	4.45
No. 8. 2–9 Base goods	2.25	2.27
	2.22	2.24
Average	2.24	2.26
No. 9. Calcium cyanamid	15.22	15.26
	15.22	15.28
	15.32	15.28
Average	15.25	15.27
General average	9.23	9.24

All of the determinations were made under the same conditions. The time of digestion was 2 hours and the digestion mixture consisted of

20 cc. of concentrated sulphuric acid, 10 grams of potassium sulphate or 10 grams of anhydrous sodium sulphate, and 1 gram of metallic mercury.

The results show in every sample that sodium sulphate gives results practically identical with those obtained with potassium sulphate. The greatest difference in any one sample is well within the experimental error, being only 0.05 per cent of ammonia in Sample 6. The general average of all samples is 9.23 per cent when potassium sulphate is used and 9.24 per cent when sodium sulphate is used.

In view of the above results, the writer concludes that sodium sulphate may be used as a substitute for potassium sulphate in the Kjeldahl-Gunning-Arnold method for the determination of ammonia in fertilizers.

INVESTIGATIONS OF THE KJELDAHL METHOD FOR DETERMINING NITROGEN.

By I. K. PHELPS (Bureau of Chemistry, Washington, D. C.), *Associate Referee on Special Study of the Kjeldahl Method*, and H. W. DAUDT[1] (Bureau of Chemistry, Washington, D. C.).

The hydrolysis of pyridin compounds and other refractory substances was discussed in the report presented to this association in 1915. It was found that the hydrolysis of pyridin zinc chlorid, approximately 0.3 gram for each analysis, was complete when the digestion continued for $2\frac{1}{2}$ hours in an open Kjeldahl flask of 500 cc. capacity with a *boiling* mixture of 25 cc. of sulphuric acid, 0.7 gram of mercuric oxid and 10 grams of potassium sulphate. When sodium sulphate was substituted for an equal weight of potassium sulphate the results obtained were below the theory, the error equaling as much as 10 per cent of the total nitrogen. Return condensers, constructed entirely of lead, placed in the neck of the flask, reduced the amount of sulphuric acid volatilized during hydrolysis, causing a more constant proportion of sulphuric acid to potassium sulphate or sodium sulphate in the presence of mercury. These served not only to prevent the vaporization of sulphuric acid, but also to retain the acid ammonium sulphate even when excessive quantities of potassium sulphate were employed. It was found that with return condensers constructed of lead the relative amounts of potassium sulphate and sulphuric acid in the presence of mercury determine the completeness of the hydrolysis. For instance, in the presence of 0.7 gram of mercuric oxid, 25 cc. of acid and 10 grams of potassium sulphate caused incomplete decomposition, but when 15 cc. of sulphuric acid were used with amounts of potassium sulphate varying from 15 to 30

[1] Present address, Jackson Laboratory, E. I. DuPont Co., Wilmington, Del.

grams, excellent results were obtained. When more potassium sulphate was employed the results were somewhat lower. Sodium sulphate seemed to give varying results.

Recent investigations show that the use of disodium phosphate or of sodium pyrophosphate, with or without condensers, in the place of potassium sulphate is undesirable. Violent bumping usually occurred before the hydrolysis had progressed sufficiently. Further, the results were variable. Experiments conducted in open flasks with the boiling mixture of 10 grams of potassium sulphate, 25 cc. of sulphuric acid and various metallic catalysts showed that the hydrolysis of pyridin zinc chlorid is complete only when 0.7 gram of mercuric oxid is present. Mercuric oxid present in the proportion of 0.2 gram is insufficient for complete hydrolysis of so refractory a compound as pyridin, even when ideal proportions of sulphuric acid and potassium sulphate are used with condensers in the neck of the flask. Copper sulphate, nickel sulphate, potassium aluminium sulphate, zinc chlorid, manganese chlorid, manganese dioxid, tungstic acid, molybdic acid, titanic acid or vanadic acid under the conditions caused incomplete hydrolysis. It is to be noted that, in the presence of 0.7 gram of mercuric oxid and the proper proportion of potassium sulphate and sulphuric acid, hydrolysis is complete without the presence of copper sulphate.

QUALITATIVE STUDY OF THE HYDROLYSIS OF AMINS.

Methylamin, trimethylamin, cholin, betain and tetramethylammonium salts were made and hydrolyzed at boiling temperature with suitable mixtures of sulphuric acid, copper sulphate, mercury, potassium or sodium sulphate. The products of hydrolysis were dissolved in water and potassium sulphid solution added if metallic catalysts had been used. This solution was made strongly alkaline with a saturated solution of sodium hydroxid and distilled into a slight excess of hydrochloric acid. In a few instances the excess of N/5 hydrochloric acid was titrated with N/10 sodium hydroxid in order to determine the amount of alkali in the distillate. Methyl red was used as indicator. The determinations were made with H. E. Woodward of the Bureau of Chemistry, according to the methods of Alsberg and Woodward[1] for detecting the presence of amins and trimethylamin. For this purpose the slightly acid solution was evaporated to a small volume and transferred to a test tube for the trimethylamin test. A normal solution of mercuric iodid in potassium iodid was carefully added from a graduated pipette until precipitation ceased. Each cubic centimeter of the reagent precipitated approximately 0.06 gram of trimethylamin, the equivalent of 0.014 gram of nitrogen. When no trimethylamin was present the solution was transferred to a small flask and distilled after making alkaline

[1] Presented under the title "A New Reagent for Volatile Tertiary Amins" at the meeting of the American Chemical Society in New York, September 1916.

with sodium hydroxid. Sodium sulphid was added with the sodium hydroxid, if the solution had been tested with the trimethylamin reagent. From 5 to 10 cc. were distilled into 10 cc. of 40 per cent formaldehyde solution in a test tube. Approximately 5 cc. of a N/4 solution of mercuric bromid in potassium bromid was then added and the test tube warmed in the steam bath. The amount of amin present was estimated by the amount of precipitate.

The hydrolysis of monomethylamin with sulphuric acid and potassium sulphate was found to proceed slowly unless the weight of potassium sulphate was equal to or greater than that of sulphuric acid. With sulphuric acid and copper sulphate or mercuric oxid, the amin was even less completely hydrolyzed. When either copper sulphate or mercuric oxid was present with 25 cc. of sulphuric acid and 10 grams of potassium sulphate, the hydrolysis was rapid. In the presence of 1 gram of copper sulphate or 0.7 gram of mercuric oxid an amount of methylamin, containing 0.07 gram of nitrogen, was almost completely converted to ammonia by boiling for 1 hour. When 10 grams of sodium sulphate were used with either of the metallic catalysts, the hydrolysis was in general almost as effective as when potassium sulphate was similarly used.

The hydrolysis of trimethylamin with sulphuric acid and potassium sulphate was found to proceed very slowly, even when the weight of potassium sulphate equalled that of the sulphuric acid. The action of either of the two metallic catalysts with 25 cc. of sulphuric acid and 10 grams of potassium sulphate was extremely slow. Trimethylamin was hydrolyzed very quickly by boiling with sulphuric acid, potassium sulphate and either of the two metallic catalysts. The larger amounts of the catalysts were more effective than the smaller amounts. The effect of mercuric oxid in the presence of potassium sulphate and sulphuric acid seemed to be slightly impaired by the presence of chlorid, only when the hydrolysis was conducted for 1 hour or less with the 0.2 gram of the catalyst. A sublimate of mercuric chlorid was noted in a number of instances. When an equal weight of sodium sulphate was used in place of potassium sulphate, the hydrolysis was not so rapid, except when 0.7 gram of mercuric oxid was present. Complete conversion to ammonia was most quickly effected by the action at boiling temperature of a mixture of 25 cc. of sulphuric acid, 10 grams of potassium or sodium sulphate, and 0.7 gram of mercuric oxid, trimethylamin, represented by 0.05 gram of nitrogen, requiring less than $1\frac{1}{2}$ hours.

Experiments were next conducted for the purpose of studying the hydrolysis of tetramethylammonium compounds, which from their constitution might be expected to yield trimethylamin.

The amounts of tetramethylammonium chlorid hydrolyzed by boiling mixtures of sulphuric acid and copper sulphate or mercuric oxid were

very small. A mixture of 10 grams of potassium sulphate and 25 cc. of sulphuric acid was somewhat more effective, but the nitrogen recovered was only 70 per cent of that recovered when 0.7 gram of mercuric oxid and 10 grams of potassium sulphate were used. No positive reactions for trimethylamin were obtained in any of the experiments, while slight positive tests for amins were obtained when potassium sulphate and sulphuric acid were used, with or without mercuric oxid.

Distillation with sodium hydroxid solution did not decompose an appreciable quantity of cholin. Hydrolysis with boiling sulphuric acid and copper sulphate or mercuric oxid took place very rapidly with the formation of large amounts of trimethylamin.

Distillation from a strongly alkaline solution did not hydrolyze an appreciable amount of betain. The action of 10 grams of potassium sulphate with 25 cc. of sulphuric acid seemed to be effective whether the metallic catalysts were present or not. The action of sulphuric acid with copper sulphate or mercuric oxid was ineffective. No trimethylamin was found in any of the experiments with betain. Moderate amounts of primary or secondary amins were found, however.

HYDROLYSIS OF CERTAIN ORGANIC COMPOUNDS.

The hydrolysis of certain organic compounds of various constitutions was reported at the annual meeting of this association in 1915. Other substances have since been studied. In the presence of 0.7 gram of mercuric oxid, 10 grams of potassium sulphate and 25 cc. of sulphuric acid weights of the compound varying from 0.2 to 0.4 gram were hydrolyzed completely by heating, without condensers, at the boiling point for $2\frac{1}{2}$ hours. The hydrolysis was found to be complete for the compounds grouped below.

Glucosamin hydrochlorid.
Tetramethylammonium derivatives:
  Tetramethylammonium iodid.
  Cholin hydrochlorid.
Pyrol derivative:
  Isatin.
Pyrolidin derivatives:
  Atropin.
  Cocain.
Pyridin derivatives:
  Nicotin zinc chlorid.
  Nicotinic acid.
Piperidin derivative:
  β-Eucaine hydrochlorid.
Quinolin derivatives:
  Hydroxyquinolin.
  Cinchonidin.
  Strychnin.
  Brucin.
Isoquinolin derivatives:
  Papaverin.
  Narcotin.
  Morphin.
  Hydrastinin.
Purin derivative:
  Caffein.
Imidazole or glyoxalin derivatives:
  Lophin.
  Amarin.
  Histidin dihydrochlorid.
Quinoxalin derivative:
  Quinoxalin hydrochlorid.
Quinazolon derivatives:
  2-Methyl 4-quinazolon.
  2-Methyl 3-phenyl 4-quinazolon.

The above procedure, with such modifications as are necessary, was applied to certain compounds containing two nitrogen atoms directly united.

THE DETERMINATION OF NITROGEN IN AZO COMPOUNDS.

It was found that azo compounds were not completely hydrolyzed to ammonia by digestion with 0.7 gram of mercuric oxid, 10 grams of potassium sulphate and 25 to 30 cc. of sulphuric acid, whether applied directly or after preliminary treatment with zinc dust, salicylic acid and sulphuric acid, with zinc dust and sulphurous acid solution or with a mixture of fuming sulphuric acid and sulphur. When the preliminary treatment included solution in 20 cc. of alcohol and reduction with zinc dust and hydrochloric acid, the results were in fair accord with the theory. The hydrochloric acid reacted so slowly with the zinc that from 0.2 to 0.4 cc. of stannous chlorid solution, consisting of 40 grams of stannous chlorid in 100 cc. of concentrated hydrochloric acid, was added to hasten the action. The mixture was kept boiling for 15 minutes or for 7 minutes after decolorization. Glass return condensers of a modified Hopkins type were placed in the neck of the flasks to prevent the evaporation of alcohol. After cooling, an equal volume of water and 30 cc. of sulphuric acid were added and the mixture heated until the water had been expelled and foaming had ceased. After the addition of 0.7 gram of mercuric oxid and 10 grams of potassium sulphate the hydrolysis was conducted at the boiling point. Reduction with stannous chlorid in alcoholic solution was more efficacious. The azo compound was dissolved in 20 cc. of alcohol, 5 cc. of stannous chlorid solution, containing 40 grams of stannous chlorid in 100 cc. of hydrochloric acid, added, and the mixture kept at the boiling point for 15 minutes if bleaching is completed in 7 minutes or less. And, if bleaching required boiling for 15 minutes or more, boiling was continued for an additional 7 minutes. Return condensers were employed to avoid the evaporation of alcohol. After cooling, an equal volume of water and 30 cc. of sulphuric acid were added and the mixture carefully heated until the water had been expelled and foaming had ceased. Then, after the addition of 0.7 gram of mercuric oxid and potassium sulphate, the hydrolysis was conducted at the boiling temperature. In some instances, where too much acid had been volatilized, the separation of stannous sulphate within the flask caused bumping. This was partly eliminated by heating after adding 5 cc. of concentrated sulphuric acid and heating until solution was again obtained. The results agreed closely with the theory. The time required for discharging the color of the azo compound is much shorter if stannous chlorid is used for reduction than if zinc and hydrochloric acid are employed. Further, the results are slightly nearer the theory.

The following compounds were investigated:

Azobenzene.	Diethyl red.
Hydroxyazobenzene.	Dipropyl red.
Amidoazobenzene.	Benzene azo, β-naphthylamin.
Toluene azo, ρ-toluidin.	Ponceau 4 R.
Methyl red.	Congo red.

DETERMINATION OF NITROGEN IN HYDRAZIN COMPOUNDS.

It was observed that hydrazin sulphate and semicarbazid hydrochlorid were not completely hydrolyzed by digestion with 0.7 gram of mercuric oxid, and 10 grams of potassium sulphate and 25 to 30 cc. of sulphuric acid, whether applied directly or after preliminary treatment with stannous chlorid or with zinc and hydrochloric acid; or, by formation of hydrazin derivatives of glucose in the presence of sodium acetate and water; or by reduction of these compounds obtained as above with stannous chlorid, sodium amalgam or sodium formate. When zinc dust and acetic acid were employed, the results indicated complete hydrolysis.

The procedure followed below seemed to be applicable to hydrazin, phenylhydrazin and phenylmethylhydrazin compounds, but not to semicarbazid or oxamazid.

The nitrogen compounds were dissolved in water; glucose, glacial acetic acid and zinc dust added in the order mentioned; and the mixture kept at the boiling temperature for 1 hour under a return condenser of the Hopkins type. Upon cooling, 30 cc. of concentrated sulphuric acid were added and the mixture carefully heated until the water had been evolved and foaming had entirely ceased. Then, after the addition of 0.7 gram of mercuric oxid and 10 grams of potassium sulphate, the hydrolysis was conducted at the boiling temperature.

The following method was found to be of more general application. Alcoholic solutions of the nitrogen compounds were treated with formaldehyde solution, zinc dust and concentrated hydrochloric acid. The mixture was kept at the boiling temperature for 30 minutes or more under a return condenser. After the reduction had progressed for 15 minutes a small quantity of stannous chlorid solution was added for the purpose of hastening the action of the acid on the zinc. After cooling, an equal volume of water and 30 cc. of sulphuric acid were added. When the water had been expelled the hydrolysis was conducted in the usual manner with mercuric oxid and potassium sulphate. The method will give results in accord with the theory, if reduction of the aldehyde nitrogen complex to the amino compound is complete. It appears that the variability in the results is due to the impurity in the zinc dust rather than to the method. It seems to be a matter of some difficulty to obtain a supply of uniformly pure zinc dust. Oxid in the free metal, hydrolyzable nitrogen containing compounds, or both, present in the

zinc dust in varying quantities, made it impossible to find a sufficiently uniform sample. It was noted that a proper state of subdivision wa also an important factor in the efficacy of the zinc when employed a the reducing agent. Following is a list of the compounds investigated

Hydrazin sulphate.
Phenylhydrazin hydrochlorid.
Bromphenylhydrazin.
Methylphenylhydrazin sulphate.
Diphenylhydrazin hydrochlorid.
ρ-Nitrophenylhydrazin.
Phenylbenzoylhydrazin.
Diphenylbenzoylhydrazin.
Semicarbazid hydrochlorid.
Phenylsemicarbazid.
Oxamazid.

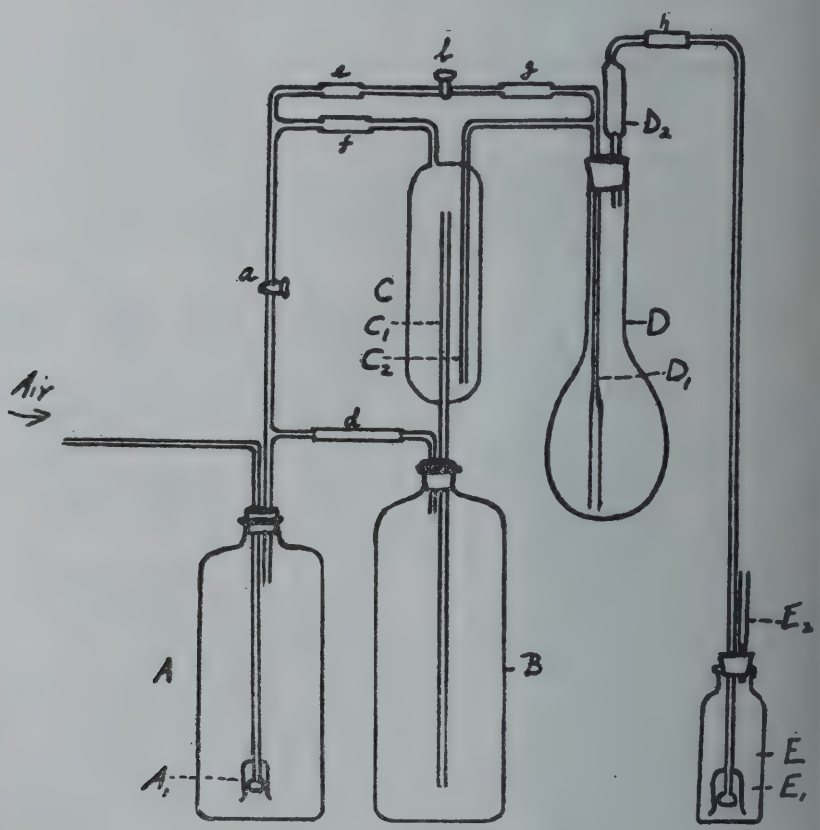


FIG. 1. AERATION APPARATUS.

A NEW AERATION APPARATUS.

The addition of saturated sodium hydroxid to a strong acid solution is controlled and the reacting mixture kept agitated by means of a divided air current, the main portion of which serves to agitate the mixture, the auxiliary portion to force over the alkaline liquid. Undue

violence of the reaction and the danger of drawing the absorbing solution into the reaction flask are obviated. By partly closing the stop-cock controlling the main air supply, a portion of the air was diverted into the sodium hydroxid reservoir, thereby forcing that solution slowly into the flask. Furthermore, it seemed desirable to have a convenient method for handling and measuring the strong alkaline solution. The apparatus is shown in Figure 1.

When the current of air is shut off at (a), sodium hydroxid solution is forced from the supply bottle (B) into the reservoir (C), the pressure being relieved through (b). After the liquid has reached a level in (C) higher than the top of (C_1), the stop-cock (a) is opened, when the level automatically falls to the top of (C_1). Now, (b) is partly closed, with the result that the sodium hydroxid in the reservoir is gradually forced into the flask through the tube (D_1), while at the same time a current of air is passing through the same tube. By opening or closing (b), the sodium hydroxid can be added at will, drop by drop, if desirable. When all of the sodium hydroxid has been added, (b) is opened full and the aeration proper is begun.

Pure ammonium sulphate was dissolved by gentle heating in various mixtures containing sulphuric acid, potassium sulphate, mercuric oxid and magnesium phosphate contained in a Kjeldahl flask. After water had been added to the contents of the flask and the apparatus connected, saturated sodium hydroxid was forced over and the ammonia aerated by means of a current of air approximating 850 liters per hour, into standard hydrochloric acid solution. A second aeration was made into fresh standard acid solution, and finally ammonia-free water was added to the contents of the reaction flask and a distillation made. In some instances the distillations were repeated after the addition of more ammonia-free water. Complete aeration and absorption of ammonia from 0.2400 gram of ammonium sulphate was secured in 25 minutes when from 15 to 20 cc. of sulphuric acid, 75 cc. of water and 125 cc. of saturated sodium hydroxid solution were employed. When 10 cc. or less of sulphuric acid were present, it was necessary to heat the mixture of sulphuric acid and water almost to the boiling point before adding the sodium hydroxid solution. When more than 25 cc. of sulphuric acid were present, complete aeration was not secured in the time indicated. The presence of as much as 0.7 gram of magnesium phosphate did not affect the results.

When pure monomethylamin sulphate prepared from acetamid was aerated in a similar manner, it was found impossible to aerate completely the volatile alkali. The equivalent of 0.0005 gram of nitrogen remained in the reaction flask and could be recovered by distillation after addition of ammonia-free water. When a mixture consisting of am-

monium sulphate and methylamin sulphate, in the proportions of their equivalent weights, and containing 0.3464 gram of nitrogen, was aerated in like manner, the aeration of the volatile acid consuming constituents was complete.

It is to be noted that when hydrolysis is conducted with a boiling mixture of 25 cc. of sulphuric acid, 10 grams of potassium sulphate and 0.7 gram of mercuric oxid, less than 25 cc. of acid are present and more than 10 cc. should be present at the end of the digestion. Further, hydrolysis of amins to ammonia has been shown to be complete in less than $1\frac{1}{2}$ hours.

Below is a summary of the advantages and disadvantages of the aeration method with the use of the above described apparatus.

The sodium hydroxid solution is added to the mixture after the apparatus has been fully and completely connected.

Bumping, which is so common when boiling strong alkaline solutions, particularly in the presence of insoluble matter and salts which separate out on boiling, is eliminated; also the use of zinc, which is added to prevent bumping.

Furthermore, the injury and breakage of flasks caused by boiling strong alkaline solutions is reduced. The danger of boiling or spraying over is entirely eliminated, for an efficient device for breaking up the spray is utilized.

The sodium hydroxid solution should be purified before use by aeration at the temperature of the steam bath, no blank for reagents being necessary in such a case. It is extremely difficult to obtain sodium hydroxid which will not yield an appreciable amount of volatile alkali on distillation. The handling of the strong sodium hydroxid solution is reduced to a minimum. Further, the solution does not come into contact with any stop-cocks or with rubber.

If hydrogen sulphid is evolved when the sodium hydroxid is added, during aeration it is completely expelled from the standard acid solution. In the distillation process whatever hydrogen sulphid escapes absorption by the alkaline solution is likely to remain in the acid solution and later affect the titration with certain indicators.

The aeration can be stopped and then continued at any time if desirable. The time of aeration can be made more definite than that of distillation. The time of actual distillation possibly can be made shorter than that of aeration, but it is done so with risk of mechanical transfer of sodium hydroxid or incomplete distillation of ammonia or both. However, the aeration method can be made to save time, because it is not necessary to cool the mixture of sulphuric acid and water before beginning the operation. Furthermore, the aeration method requires little attention between the time of starting and that of finishing.

Compressed air is not always available, but with few modifications the above apparatus can be adapted for suction. A good water pump will provide suction strong enough for several units.

The use of burners and condensers is entirely eliminated.

REPORT ON POTASH.

By T. D. JARRELL[1] (College of Agriculture, College Park, Md.), *Associate Referee.*

The association at its last meeting recommended the following work for the determination of potash:

(1) That further cooperative work on the perchlorate method for the determination of potash be discontinued for the present, but the succeeding referee be advised to continue the investigation of the method with a view to perfecting the working details.

(2) That further work be done on the method for obtaining water-soluble potash to determine whether hydrochloric acid shall or shall not be used before the precipitation with ammonium hydroxid and ammonium oxalate is made.

The following instructions were sent to collaborators:

Determine potash on as many of your own samples as possible by the following methods:

(*A*) *Official Lindo-Gladding Method.*

Use the process for preparing the water extract as adopted officially in 1912[2].

(*B*) *Modified Official Method.*

This is the same as (*A*) with the exception that the addition of 2 cc. of concentrated hydrochloric acid to water extract and boiling is omitted. After washing 2.5 grams on filter paper, add directly to the hot solution ammonium hydroxid and ammonium oxalate and proceed as in the official Lindo-Gladding method.

PART I.—RESULTS OF COLLABORATIVE WORK.

The following table presents a comparison of results obtained upon analyzing solutions of potash prepared according to the official method with those obtained on the same samples when solution was effected by the modified official method.

---

[1] Present address, Bureau of Chemistry, Washington, D. C.
[2] U. S. Bur. Chem. Bull. **152**: 41; **162**: 48.

TABLE 1.

Effect of hydrochloric acid.

COLLABORATOR	NUMBER OF SAMPLES REPORTED	AVERAGE POTASSIUM OXID OFFICIAL METHOD	AVERAGE POTASSIUM OXID MODIFIED OFFICIAL METHOD
		per cent	*per cent*
L. E. Westman, Laboratory of the Inland Revenue Department, Ottawa, Canada	5	2.97	2.95
S. E. Asbury, College Station, Texas	12	1.17	1.15
H. C. Moore, Armour Fertilizer Works, Atlanta, Ga.	10	3.57	3.57
I. D. Sessums, Agricultural College, Miss.	5	1.67	1.61
E. G. Proulx, Agricultural Experiment Station, La Fayette, Ind.	8	8.93	8.86
Average for 40 samples		3.66	3.65

The table gives the average results obtained by each collaborator, and a large range of fertilizer materials is represented. E. E. Vanatta (University of Missouri, Columbia, Mo.), working on sixty-six samples of commercial fertilizers, found thirty-four higher by adding hydrochloric acid, thirty higher by omitting hydrochloric acid, and no variation with two samples.

DISCUSSION.

The average of all results reported shows 3.66 per cent potassium oxid by adding hydrochloric acid to potash solution and 3.65 per cent potassium oxid by omitting it. Of the forty samples reported, twenty-four yield a slightly higher result by adding hydrochloric acid; thirteen, a slightly higher result by omitting hydrochloric acid. The results are the same on three samples. The difference between the two methods on every sample appears to be within the limit of the usual error of manipulation. The work of the past three or four years has shown that the addition of hydrochloric acid to the potash solution does not give higher results.

It is recommended—

That the official method for the preparation of potash solution in mixed fertilizers[1] be revised to read as follows:

Place 2.5 grams of the sample upon a 12.5 cm. filter paper and wash with successive portions of boiling water into a 250 cc. graduated flask until the filtrate amounts to about 200 cc. Add to the hot solution a slight excess of ammonium hydroxid and sufficient ammonium oxalate to precipitate all the lime present, cool, dilute to 250 cc., mix, and pass through a dry filter.

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 12.

PART II.—THE PERCHLORATE METHOD.

For the purpose of testing the accuracy of the perchlorate method against potassium chlorid and potassium sulphate of tested purity, as well as mixtures of these salts with substances usually present in fertilizers, solutions of the composition indicated in Table 2 were prepared. Analysis was performed according to the following methods:

Method I.

(Solutions A to I.)

Place 20 cc. of the solution in an evaporating dish, add 5 cc. of perchloric acid (sp. gr. 1.12), evaporate on steam or sand bath until heavy fumes are emitted, take up the residue with 5 cc. of water, add 5 cc. of perchloric acid, and again evaporate until all free hydrochloric acid is driven off and dense white fumes of perchloric acid appear. (If the solution goes to dryness and a hard mass remains, take up with a few drops of perchloric acid.) When the evaporation is made on a water bath, place dish on hot plate and heat carefully until all hydrochloric acid is expelled. After cooling add 20 cc. of 95% alcohol and stir well. Allow to stand for 30 minutes. Decant the alcohol through a Gooch crucible having a fairly thick pad ($\frac{1}{8}$ inch) and wash twice by decantation with 95% alcohol containing 0.2% perchloric acid[1]. Transfer the precipitate to crucible with the 95% alcohol containing perchloric acid and wash until the filtrate amounts to 75 or 80 cc. Finally, to wash out all perchloric acid, wash twice with alcohol-ether (1 part 95% alcohol to 1 part ethyl ether) using 3–5 cc. each time. Dry for 30 minutes at 120–130°C. and weigh. Dissolve the potassium perchlorate from the Gooch crucible with about 200 cc. of hot water and dry to constant weight in air oven. Cool and weigh. Loss in weight is potassium perchlorate.

Method II.

(Solutions J and K.)

Place 20 cc. of the solution in a porcelain or silica dish (do not use platinum), add an excess of 3% barium hydroxid solution and without filtering evaporate to dryness on sand bath. Ignite the residue below redness for 10 minutes over a Bunsen burner. Extract the residue with 20 cc. of boiling water, breaking up the material as much as possible. Filter into an evaporating dish of about 175 cc. capacity, and wash with boiling water until the filtrate amounts to 125–150 cc. Add 5 cc. of perchloric acid, evaporate carefully on sand bath until it fumes strongly, take up with 5 cc. of water, add a second 5 cc. of perchloric acid, evaporate, cool, and proceed in accordance with Method I.

Method III.

(Solution K.)

Transfer 20 cc. to a platinum dish and proceed according to the official Lindo-Gladding method[2] until after the addition of 1 cc. of sulphuric acid (1 to 1) and ignition. Dissolve the residue in about 25 cc. of hot water, add about 2 cc. of concentrated hydrochloric acid and add in slight excess a 10% barium chlorid solution acidified with hydrochloric acid. Add the barium chlorid solution at the rate of about 1 drop per second. Filter[3] into an evaporating dish and wash the precipitate and filter paper thoroughly with hot water. Add perchloric acid and proceed as outlined in Method I.

[1] Made by adding 1 cc. of perchloric acid (sp. gr. 1.12) to 100 cc. of 95% alcohol.
[2] *Assoc. Official Agr. Chemists. Methods*, 1916, 13.
[3] After precipitating with barium chlorid, it is often necessary to allow the hot solution to stand a short time to insure a precipitate which filters well and gives a clear filtrate.

TABLE 2.

Effect of added salts upon the determination of potash as potassium perchlorate.

SOLUTION (Made up to 1000 cc.)	POTASSIUM PERCHLORATE FOUND	POTASSIUM OXID TAKEN	POTASSIUM OXID FOUND	ERROR POTASSIUM OXID	ERROR POTASSIUM OXID
	gram	*gram*	*gram*	*mg.*	*per cent*
A	0.3703	0.1263	0.1259	−0.4	99.68
	0.3717	0.1263	0.1264	+0.1	100.08
Potassium chlorid, 10 grams	0.3707	0.1263	0.1260	−0.3	99.76
	0.3706	0.1263	0.1260	−0.3	99.76
	0.3711	0.1263	0.1262	−0.1	99.92
	0.3718	0.1263	0.1264	+0.1	100.08
Average	-----	-----	-----	----	99.88
B	0.3711	0.1263	0.1262	−0.1	99.92
	0.3722	0.1263	0.1265	+0.2	100.16
Potassium chlorid, 10 grams; sodium chlorid, 15 grams	0.3721	0.1263	0.1265	+0.2	100.16
	0.3706	0.1263	0.1260	−0.3	99.76
	0.3705	0.1263	0.1260	−0.3	99.76
	0.3704	0.1263	0.1259	−0.4	99.68
Average	-----	-----	-----	----	99.89
C	0.3704	0.1263	0.1259	−0.4	99.68
Potassium chlorid, 10 grams; magnesium chlorid, 10 grams	0.3724	0.1263	0.1266	+0.3	100.24
	0.3720	0.1263	0.1265	+0.2	100.16
Average	-----	-----	-----	----	100.02
D	0.3703	0.1263	0.1259	−0.4	99.68
	0.3731	0.1263	0.1269	+0.6	100.48
Potassium chlorid, 10 grams; calcium carbonate (dissolved in dilute hydrochloric acid), 10 grams	0.3724	0.1263	0.1266	+0.3	100.24
	0.3697	0.1263	0.1255	−0.8	99.37
	0.3711	0.1263	0.1262	−0.1	99.92
	0.3725	0.1263	0.1267	+0.4	100.32
Average	-----	-----	-----	----	100.02
E	0.3715	0.1263	0.1263	0.0	100.00
	0.3724	0.1263	0.1266	+0.3	100.24
Potassium chlorid, 10 grams; disodium phosphate, 10 grams	0.3724	0.1263	0.1266	+0.3	100.24
	0.3708	0.1263	0.1261	−0.2	99.84
	0.3718	0.1263	0.1264	+0.1	100.08
	0.3711	0.1263	0.1262	−0.1	99.92
Average	-----	-----	-----	----	100.05
F	0.3718	0.1263	0.1264	+0.1	100.08
	0.3689	0.1263	0.1254	−0.9	99.29
Potassium chlorid, 10 grams; barium chlorid, 10 grams	0.3695	0.1263	0.1256	−0.7	99.45
	0.3696	0.1263	0.1257	−0.6	99.53
	0.3709	0.1263	0.1261	−0.2	99.84
Average	-----	-----	-----	----	99.64

TABLE 2.—Concluded.

SOLUTION (Made up to 1000 cc.)	POTASSIUM PERCHLORATE FOUND	POTASSIUM OXID TAKEN	POTASSIUM OXID FOUND	ERROR POTASSIUM OXID	ERROR POTASSIUM OXID
	gram	*gram*	*gram*	*mg.*	*per cent*
G	0.3716	0.1263	0.1263	0.0	100.00
	0.3722	0.1263	0.1265	+0.2	100.16
Potassium chlorid, 10 grams; sodium chlorid, 15 grams; magnesium chlorid, 10 grams	0.3699	0.1263	0.1258	−0.5	99.61
	0.3716	0.1263	0.1263	0.0	100.00
	0.3730	0.1263	0.1268	+0.5	100.40
Average	-----	-----	-----	----	100.03
H					
Potassium chlorid, 10 grams; sodium chlorid, 15 grams; magnesium chlorid, 10 grams; calcium carbonate (dissolved in dilute hydrochloric acid), 10 grams	0.3730	0.1263	0.1268	+0.5	100.40
	0.3703	0.1263	0.1259	−0.4	99.68
	0.3730	0.1263	0.1268	+0.5	100.40
	0.3731	0.1263	0.1269	+0.6	100.48
	0.3708	0.1263	0.1261	−0.2	99.84
Average	-----	-----	-----	----	100.16
I	0.1555	0.0541	0.0529	−1.2	97.78
	0.1556	0.0541	0.0529	−1.2	97.78
Potassium sulphate, 5 grams; concentrated hydrochloric acid, 10 cc.; barium chlorid in slight excess	0.1563	0.0541	0.0531	−1.0	98.16
	0.1566	0.0541	0.0532	−0.9	98.34
	0.1571	0.0541	0.0534	−0.7	98.71
	0.1554	0.0541	0.0528	−1.3	97.60
Average	-----	-----	-----	----	98.06
J[a]					
Potassium chlorid, 2.5 grams; potassium sulphate, 2.5 grams; magnesium sulphate, 2.5 grams; sodium chlorid, 5 grams; acid phosphate (water extracted), 9 grams	0.1701	0.0586	0.0578	−0.8	98.63
	0.1724	0.0586	0.0586	0.0	100.00
	0.1732	0.0586	0.0589	+0.3	100.51
	0.1717	0.0586	0.0584	−0.2	99.66
	0.1729	0.0586	0.0588	+0.2	100.31
	0.1720	0.0586	0.0585	−0.1	99.91
Average	-----	-----	-----	----	99.84
K[b]	0.1704	0.0586	0.0579	−0.7	98.81
Potassium chlorid, 2.5 grams; potassium sulphate, 2.5 grams; magnesium sulphate, 2.5 grams; sodium chlorid, 5 grams; acid phosphate (water extracted), 9 grams; concentrated hydrochloric acid, 8 cc.	0.1698	0.0586	0.0577	−0.9	98.47
	0.1705	0.0586	0.0580	−0.6	98.98
	0.1704	0.0586	0.0579	−0.7	98.81
	0.1713	0.0586	0.0582	−0.4	99.32
	0.1719	0.0586	0.0584	−0.2	99.66
	Average	-----	-----	----	99.01
	0.1705	0.0586	0.0578	−0.8	98.63
	0.1723	0.0586	0.0586	0.0	100.00
	0.1707	0.0586	0.0580	−0.6	98.98
	0.1729	0.0586	0.0588	+0.2	100.31
	0.1722	0.0586	0.0585	−0.1	99.91
	0.1708	0.0586	0.0581	−0.5	99.15
Average	-----	-----	-----	----	99.50

[a] Ammonium hydroxid and ammonium oxalate were not added to this solution.
[b] Ammonium hydroxid and ammonium oxalate were added to this solution as per official method.

DISCUSSION.

The method used last year for washing the potassium perchlorate in the Gooch crucible has been modified. Since it was found that the use as a wash of 95 per cent alcohol saturated with potassium perchlorate often gives high results, due to deposition from the alcohol of some potassium perchlorate upon both the crucible and the potassium perchlorate, the washing was made in all determinations considered in this report with 95 per cent alcohol containing 0.2 per cent of perchloric acid; 50 to 60 cc. of alcohol were used and the precipitate washed twice with 3 to 5 cc. portions of alcohol-ether (1 to 1) to remove the last traces of perchloric acid.

The associate referee verified the findings of Davis[1] that 50 cc. of 95 per cent alcohol dissolve 0.0065 to 0.0085 gram of potassium perchlorate. By washing out the last traces of perchloric acid with alcohol-ether the loss is reduced to 0.0015 to 0.0020 gram of potassium perchlorate for each 50 cc. of wash. Alcohol containing 0.2 per cent of perchloric acid dissolves about 0.0015 gram of potassium perchlorate per 50 cc. It would appear, therefore, that the best results are to be obtained by a proper balancing of errors. In order that uniformity of results may be secured, a definite set of conditions must be followed most carefully. When washing with alcohol containing 0.2 per cent of perchloric acid, the quantity of alcohol used must be definitely set, and perchloric acid sufficient to combine with all bases present must be added.

In a recent article Davis[2] has shown by experimental data that when potassium sulphate is evaporated directly with perchloric acid accurate results are obtained so long as perchloric acid remains in large excess. The associate referee used the procedure suggested by Davis without success, all results being very high.

Under Solution I, Table 2, are shown the results obtained on potassium sulphate after precipitation of the sulphate with barium chlorid. All results are low, which is probably due to the occlusion of some potash by the barium sulphate.

The barium hydroxid process (Method II) has the following advantages over the barium chlorid process (Method III): (1) All ammonium salts are volatilized as ammonia. (2) Since magnesium salts are precipitated as magnesium hydroxid, the addition of sufficient perchloric acid to combine with all the magnesium is not required. (3) Soluble silicates are precipitated as barium silicate by the barium hydroxid. (4) The barium hydroxid method is shorter than treatment with sulphuric acid, burning and precipitation of sulphate with barium chlorid.

---

[1] *J. Agr. Sci.*, 1912, **5**: 64.
[2] *J. Chem. Soc.*, 1915, **107**: 1678.

CONCLUSIONS.

The perchlorate method for the determination of potash in potash salts and mixed fertilizers is quite accurate after the analyst has become acquainted with the details of manipulation.

If sufficient perchloric acid is added, phosphates and sodium, magnesium and calcium salts produce no error.

Sulphate and ammonium ions produce an error and must be removed before adding perchloric acid.

After extracting the potash from mixed fertilizers with hot water, the addition of ammonium hydroxid and ammonium oxalate is not necessary.

RECOMMENDATION.

It is recommended that the referee next year study further the barium hydroxid process of the perchlorate method on mixed fertilizers of known potash content.

The following is an incomplete bibliography of the recent literature on the perchlorate method:

J. Am. Chem. Soc., 1914, **36:** 2085.
J. Agr. Sci., 1912, **5:** 52.
Mining Eng. World, 1912, **36:** 605.
Z. landw. Versuchsw., 1915, **18:** 77.
J. Chem. Soc., 1915, **107:** 361.
Landw. Vers.-Sta., 1912, **78:** 179.
Ibid., 1915, **87:** 365.
Analyst, 1916, **41:** 165.
J. Chem. Soc., 1915, **107:** 1678.

THE SEPARATION AND GRAVIMETRIC ESTIMATION OF POTASSIUM.

By S. B. KUZIRIAN[1] (Agricultural Experiment Station, Ames, Ia.).

Sérullas[2] in 1831 proposed that the insolubility of potassium perchlorate in concentrated alcoholic solution be employed for the estimation of potassium. His method, however, received scant attention for the reason that no convenient method existed prior to 1912 for the preparation of perchloric acid. Recently Willard[3] has developed a procedure by which pure perchloric acid is produced with comparative ease.

Cooperative work by T. D. Jarrell[4] indicated that the perchlorate

[1] Present address, Box 87, Jamaica, N. Y.
[2] *Ann. chim. phys.*, 1831, **46:** 294.
[3] *J. Am. Chem. Soc.*, 1912, **34:** 1480.
[4] *J. Assoc. Official Agr. Chemists*, 1915, **1:** 400.

method in its present form is very unsatisfactory. Hill[1] has shown that anilin perchlorate, prepared easily from anilin oil and perchloric acid, has a definite composition and contains no water of crystallization. A known weight of the crystals dissolved in a measured quantity of absolute alcohol will, according to Hill, precipitate potassium quantitatively as perchlorate. A negative error of 0.0004 gram potassium oxid, or 1.5 per cent, was explained by Hill on the ground of an incomplete conversion of potassium chlorid to potassium perchlorate.

The best results are obtained by this method when the following precautions are taken. No alcohol more dilute than 99.5 per cent should be used; for every 1.5 cc. of water used for dissolving the mixed chlorids, 50 cc. of absolute alcohol should be added. A definite weight of anilin perchlorate is dissolved in 50 cc. of absolute alcohol and the solution added to the dissolved chlorids drop by drop with constant shaking and the mixture allowed to stand one hour before filtration. Under these conditions the following results were obtained:

Precipitation of potassium[a] with anilin perchlorate.

WEIGHT OF POTASSIUM CHLORID TAKEN	CORRESPONDING WEIGHT CALCULATED		WEIGHT OF POTASSIUM PERCHLORATE FOUND	CORRESPONDING WEIGHT FOUND		ERROR IN POTASSIUM OXID (LOSS)
	Potassium oxid	Potassium perchlorate		Potassium chlorid	Potassium oxid	
gram	*gram*	*gram*	*gram*	*gram*	*gram*	*gram*
0.2005	0.1266	0.3726	0.3670	0.1975	0.1247	0.0019
0.2005	0.1266	0.3726	0.3685	0.1983	0.1252	0.0014
0.2000	0.1263	0.3717	0.3675	0.1978	0.1249	0.0014
0.2000	0.1263	0.3717	0.3670	0.1975	0.1247	0.0016
0.2000	0.1263	0.3717	0.3677	0.1979	0.1250	0.0013
0.2000	0.1263	0.3717	0.3676	0.1978	0.1249	0.0014
0.2000	0.1263	0.3717	0.3690	0.1986	0.1255	0.0008
0.2000	0.1263	0.3717	0.3680	0.1980	0.1251	0.0012
0.1000	0.0632	0.1858	0.1844	0.0992	0.0627	0.0005
0.1000	0.0632	0.1858	0.1840	0.0990	0.0625	0.0007
0.1000	0.0632	0.1858	0.1845	0.0993	0.0627	0.0005
0.1000	0.0632	0.1858	0.1843	0.0992	0.0627	0.0005

[a] The potassium chlorid used was recrystallized from the commercial C. P. product. When it was estimated as chloroplatinate, it showed a purity of 99.9 per cent potassium chlorid.

[1] *Am. J. Science*, 1915, 4th ser., **40**: 75.

The substitution of anilin perchlorate for perchloric acid shortens the process considerably. It also affords the best means for direct estimation of sodium in the filtrate.

It has been the writer's experience that some potassium chlorid is occluded by the perchlorate precipitate. Three series of four experiments each were conducted to establish this fact. When the precipitant, dissolved in the proper amount of alcohol, was added all at once and filtration completed within 15 minutes, the results were considerably below the theory. When, however, the precipitant was added drop by drop with constant shaking and the mixture allowed to stand about 2 hours before filtration, the results were decidedly better.

Sulphates must be removed with barium chlorid. Unless the filtrate is to be used for the determination of sodium, the excess of barium chlorid does not interfere, provided enough of the precipitant is added to combine with all the bases present.

In the opinion of the writer, anilin perchlorate is the best reagent to replace the highly expensive platinic chlorid. It is easily prepared and the manipulation is simple. For this reason it is recommended that further collaborative work be performed and that the latest work on the use of anilin perchlorate be thoroughly tested by the collaborators.

A paper on the "Availability of Potash in Wood Ashes"[1] was presented by Messrs. R. E. Stallings and S. H. Wilson of the Georgia Department of Agriculture, Atlanta, Georgia.

A STUDY OF THE AVAILABILITY OF POTASH IN COMMERCIAL WOOD ASHES.

By R. E. Rose (State Chemist, Tallahassee, Fla.).

An unusually large number of samples of wood ashes has been analzyed by the Florida State Laboratory during the last two years. An examination of the results shows that seldom is more than 4 per cent of water-soluble potash found; frequently less than 0.5 per cent is found. Table 1 exhibits a number of analyses.

Among dealers and commercial and official chemists there has been considerable discussion of the methods employed to determine the availability or solubility of the potash in ashes. It has been claimed by some that the official method of this association for ashes—the water-soluble method—is unfair to the dealer or manufacturer, and that the Dyer method, 1 per cent citric acid solution[2] or a modification thereof would show a larger percentage of available potash.

[1] *Am. Fertilizer*, 1917, **46**: 24.
[2] H. W. Wiley. Principles and Practice of Agricultural Analysis. 2nd ed., 1908, **2**: 533.

TABLE 1.

Determinations on samples of wood ashes.

DESCRIPTION OF SAMPLE	POTASH	SAND	CARBONATE OF LIME
COMMERCIAL HARDWOOD ASHES	*per cent*	*per cent*	*per cent*
Canadian hardwood ashes	2.72	32.73	63.64
Ashes	1.47	27.99	70.50
Cypress ashes	0.61	19.27	78.22
Hardwood ashes	2.93	3.75	93.32
Ashes	0.43	78.15	21.42
Cypress ashes	0.36	18.20	80.84
Ashes	0.90	28.26	70.84
Ashes	0.48	83.98	15.54
Hardwood ashes	3.22	71.55	25.23
Hardwood ashes	1.61	23.00	75.39
Hardwood ashes	1.27	22.20	76.53
Ashes No. 1	3.37	8.02	88.61
Ashes	3.29	9.00	87.71
Hardwood ashes	0.86	46.16	34.78
Ashes	4.37	39.77	55.86
Ashes	3.42	20.66	76.00
Ashes	0.26	5.11	94.63
Ashes	1.81	22.11	76.08
Ashes No. 2	0.96	74.15	25.00
Ashes	0.28	23.20	76.52
Average	1.73	32.86	64.33
COMMERCIAL PALMETTO ASHES			
Saw Palmetto ashes	0.49	96.39	3.12
Palmetto root ashes	0.24	94.20	5.56
Palmetto ashes	1.07	-----	-----
Palmetto ashes	0.25	96.30	2.90
Palmetto ashes	1.44	-----	-----
Palmetto root ashes	4.04	81.00	15.00
Palmetto ashes	2.33	77.20	20.47
Palmetto ashes	0.57	-----	-----
Palmetto ashes	5.73	-----	-----
Palmetto ashes	2.35	-----	-----
Palmetto ashes	3.35	-----	-----
Palmetto ashes	0.51	-----	-----
Average	1.86	89.20	9.41

In order to evaluate these claims, the Florida State Laboratory made a comparison of the methods for the determination of potash in wood ashes. Seven samples were analyzed by the following methods:

(1) *Official Lindo-Gladding Method*[1].—This method was employed with these modifications. A solution of platinic chlorid was used of such dilution that 1 cc. completely precipitated 1 per cent of potash (K_2O) on the basis of a 1 gram sample. The weight of the potassium platinic chlorid was obtained by the difference between the weight of the crucible with the precipitate and that obtained after washing thoroughly with boiling water, followed by alcohol.

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 12.

(2) *Hydrochloric acid-soluble potash.*—Weigh 10 grams of the sample into a 500 cc. volumetric flask, add 50 cc. of hydrochloric acid (1 to 1), boil for 30 minutes, dilute with hot water to about 300 cc., add an excess of ammonium hydroxid and ammonium oxalate, and proceed according to the official method.

(3) *Dyer Method, potash soluble in 1% citric acid solution.*—Weigh 10 grams of the sample into a 500 cc. graduated flask, add 100 cc. of 1% citric acid solution. Stopper securely and digest at room temperature for 7 days with frequent shaking. Dilute to about 300 cc. with water, heat to boiling, add an excess of ammonium hydroxid and ammonium oxalate, and proceed as in the official method.

(4) *Modified Dyer Method.*—Use 250 cc. of 1% citric acid solution for each gram of sample and proceed in accordance with the Dyer method.

TABLE 2.

Comparison of methods of potash determination.

DESCRIPTION OF SAMPLE	HYDROCHLORIC ACID SOLUTION	ASSOCIATION METHOD	DYER METHOD	MODIFIED DYER METHOD	INSOLUBLE MATTER SAND (SiO_2)	CARBONIC ACID RADICLE
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	
Wood ashes	2.92	1.47	1.45	2.50	27.99	Large
Palmetto ashes	0.23	0.24	0.23	0.19	94.20	Small
Palmetto ashes	1.98	1.70	1.62	1.32	-----	Small
Wood ashes	5.35	4.37	4.23	4.62	38.77	Large
Palmetto ashes	4.71	4.73	4.60	3.14	81.00	Moderate
Wood ashes	0.31	0.28	0.27	0.31	23.20	Large
Wood ashes	3.61	3.30	3.22	2.77	28.25	Large
Feldspar[a]	0.02	----	0.07	0.06	-----	---------
Average	2.73	2.30	2.23	2.12	49.07	---------

[a] Not included in average.

A study of the table indicates that the potash contained in commercial wood ashes is largely in the form of potassium carbonate and that very little, if any, exists in the form of silicate. This is shown in the samples having a large proportion of insoluble matter, largely silica, and a low percentage of potash. In these samples the tendency to form silicates would be greatest, and the water-soluble potash would be less than the acid-soluble. This, however, is not the case, the water-soluble potash agreeing with the acid-soluble in every case.

CONCLUSIONS.

A close comparison of the results obtained by using the four methods of solution shows:

(1) Hydrochloric acid-soluble potash is uniformly higher than water-soluble.

(2) Results for water-soluble potash are consistently higher than those obtained by the Dyer method; also results by the method of this association are much more concordant than those by the Dyer method.

It appears that the potash in commercial fertilizers is not more soluble in dilute citric acid solution than in boiling water. Apparently nothing would be gained by substituting either the Dyer method or the modified Dyer method for the official procedure in the determination of the available potash in commercial wood ashes.

The analytical work in connection with this paper was performed by Mr. L. Heimberger, fertilizer chemist of the Florida State Laboratory.

No report was presented on soils by the referee.

Messrs. T. E. Keitt and C. J. King (Agricultural Experiment Station of Clemson Agricultural College, Clemson College, S. C.) presented a paper[1] on "A New, Rapid and Accurate Method for Estimating Lime and Potash in Soils".

NITROGENOUS COMPOUNDS IN SOILS.

By C. B. LIPMAN (Agricultural Experiment Station, Berkeley, Cal.), *Associate Referee.*

A collaborative study of the determination of nitrogen in soils was made. The official Kjeldahl method for nitrogen in soils[2], the official method for nitrogen in fertilizers[3], and the Hibbard method, as modified by the associate referee on nitrogenous compounds in soils, were investigated.

Three main samples were chosen for collaborative work: (1) Light sandy soil; (2) light clay loam; (3) heavy brown clay adobe. Of each sample three subdivisions were made in the following manner: (A) Sifted through 1 mm. sieve and dried at 100°C.; (B) leached free from nitrates and dried at 100°C.; (C) sifted through 1 mm. sieve, 0.0200 per cent of nitrogen in the form of sodium nitrate added, carefully mixed and dried at 100°C.

DISCUSSION OF RESULTS.

The figures given in Table 1 are very disappointing in some respects and very illuminating in others. An almost invariable lack of agreement between duplicate and triplicate determinations, and also among numerous repetitions, is fully brought out in the extremes reported and emphasizes the fact that no method herein studied seems to be accurate enough from the *absolute* standpoint to permit of the exact determination of small changes in the nitrogen content of soils. Attention need only be called to the great discrepancy between the nitrogen content of

[1] S. C. Agr. Expt. Sta. Bull. 188.
[2] *Assoc. Official Agr. Chemists, Methods*, 1916, 21.
[3] *Ibid.*, 8.

1A and 1B as determined by Mr. McLean and Mr. Roberts and the discrepancy frequently found between the determinations in the case of either analyst. These facts are not to be accounted for by lack of accuracy on their part, but merely emphasize the inherent differences between duplicate samples and the difficulty of duplicating digestion and distillation.

TABLE 1.

Comparative results of nitrogen determinations in soils.

NUMBER	KJELDAHL METHOD				HIBBARD METHOD				MODIFIED KJELDAHL		
	Mc Lean[a]	Pfanstile[b]	Hardy[c]	Roberts[d]	Mc Lean	Pfanstile	Hardy	Roberts	Mc Lean	Hardy	Roberts
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1A	0.0174	0.0167	0.0169	0.0270	0.0139	0.0157	0.0186	0.0260	0.0190	0.0200	0.0270
	0.0185	0.0137	0.0172	0.0260	0.0210	0.0140	0.0193	0.0260	0.0184	0.0214	0.0270
1B	0.0200	0.0162	0.0181	0.0280	0.0165	0.0169	0.0176	0.0280	0.0209	0.0179	0.0280
	0.0197	0.0152	0.0179	0.0290	0.0200	0.0157	0.0225	0.0290	0.0217	0.0234	0.0250
1C	0.0347	0.0277	0.0388	0.0390	0.0301	0.0287	0.0295	0.0390	0.0390	0.0300	0.0450
	0.0332	0.0322	0.0350	0.0390	0.0369	0.0304	0.0300	0.0390	0.0405	0.0353	0.0440
2A	0.0864	0.0792	[e]	0.0850	0.0864	0.0815	0.0939	0.0850	0.0830	0.0844	0.0930
	0.0879	0.0762	[e]	0.0860	0.0901	0.0801	0.0947	0.0860	0.0849	0.0858	0.0760
2B	0.0890	0.0822	[e]	0.0900	0.0883	0.0791	0.0847	0.0880	0.0922	0.0877	0.0890
	0.0892	0.0767	[e]	0.0910	0.0914	0.0843	0.0906	0.0890	0.0926	0.0906	0.0830
2C	0.1014	0.0932	[e]	0.0940	0.0987	0.0969	0.1021	0.0940	0.1081	0.1013	0.0970
	0.1033	0.0912	[e]	0.0950	0.1032	0.0913	0.1043	0.0940	0.1076	0.1016	0.1000
3A	0.1149	0.1062	[e]	0.0990	0.1097	0.1008	0.1164	0.1020	0.1061	0.1121	0.1120
	0.1138	0.1042	[e]	0.1010	0.1195	0.1043	0.1160	0.1030	0.1076	0.1146	0.1120
3B	0.1149	0.1107	[e]	0.1110	0.1169	0.1022	0.1115	0.1080	0.1161	0.1121	0.1080
	0.1144	0.1052	[e]	0.1130	0.1203	0.1008	0.1141	0.1080	0.1173	0.1171	0.1090
3C	0.1265	0.1212	[e]	0.1140	0.1267	0.1158	0.1286	0.1140	0.1327	0.1271	0.1250
	0.1296	0.1192	[e]	0.1160	0.1314	0.1190	0.1349	0.1150	0.1327	0.1298	0.1320

[a] Agricultural Experiment Station, New Brunswick, N. J.
[b] Agricultural Experiment Station, Lexington, Ky.
[c] Agricultural Experiment Station, Knoxville, Tenn.
[d] Agricultural Experiment Station, Berkeley, Cal.
[e] Satisfactory digestions not obtained because of going dry.

There seems to be no great difference in the results obtained by the Kjeldahl and Hibbard methods. The Kjeldahl method modified to include nitrates gives sometimes better and sometimes poorer results than either of the other methods, showing higher results on soils to which nitrate has been added, but failing to recover quantitatively the added 0.020 per cent of nitrate nitrogen.

REMARKS.

The associate referee deplores the situation with reference to the lack of cooperation or somewhat half-hearted cooperation offered by our agricultural chemists. This is not said in disparagement of the efforts of those who acted as collaborators, but with reference to those who have let the associate referee go on hoping for a year or more that the work would be completed and finally failed to submit any results.

This condition perhaps is not due to anything wrong with individuals, but rather with experiment station organizations, and the associate referee must, therefore, urge upon you the necessity of adopting some different system for studying analytical methods. Many of the good soil chemists of today employ methods in their work which they have adopted without official test, but which seem to them superior, and, in all probability are far superior, to those which are in our books as official. The reason for this is that the association has not kept abreast of the great progress of soil science, and that we are of no assistance in the improvement of methods for the use of soil chemists. It is therefore suggested that our system of work as in vogue today be changed for purposes of expedition and increased output on the testing of methods by getting experiment stations officially to carry out the testing of methods as a regular research project, so that results may be called for and expected.

The results do not, in the opinion of the associate referee, justify recommendations for the adoption of any new method, but he feels that the present official and unofficial methods for the determination of nitrogen in soils are unsatisfactory, and it is suggested that the official Kjeldahl method modified to include nitrates be discarded and that both the official Kjeldahl and Hibbard methods be further studied. It is also suggested that nitrate nitrogen be determined only by the colorimetric and reduction methods.

RECOMMENDATIONS.

It is recommended—

(1) That the association take steps towards having the experiment stations carry out officially the testing of methods as a regular research project.

(2) That further and more complete investigation be made of official and unofficial methods for the determination of nitrogen in soils.

REPORT ON INORGANIC PLANT CONSTITUENTS[1].

By Andrew J. Patten (Agricultural Experiment Station, E. Lansing, Mich.), *Referee.*

The work of the past year has been confined, for the most part, to a study of McCrudden's[2] method, which provides for the precipitation of calcium as oxalate in a boiling solution containing a small amount of hydrochloric acid. It was thought that McCrudden's method of precipitating calcium would overcome the error introduced by the occlusion of manganese, but this proved not to be the case. However, by titrating the calcium oxalate precipitate with standard permanganate solution, this source of error appears to be eliminated.

Colorimetric methods for the determination of manganese have also been studied, and potassium periodate has been selected as the most satisfactory oxidizing medium. The color developed by its use is of the same shade as the standard, which, in our experience, is not always the case with other oxidizing agents.

We used a composite solution made from the following substances in the proportions stated:

	per cent
Phosphoric acid (P_2O_5)	45.0
Calcium oxid (CaO)	3.0
Magnesium oxid (MgO)	10.0
Mangano-manganic oxid (Mn_3O_4)	0.2
Ferric oxid (Fe_2O_3)	1.5
Aluminic oxid (Al_2O_3)	1.3
Potassium oxid (K_2O)	25.0
Sodium oxid (Na_2O)	14.0
Total	100.0

The methods studied are as follows:

CALCIUM.

Dilute an amount of solution representing 0.5 gram of ash to 200 cc., add a few drops of alizarin and make slightly ammoniacal. Now add very dilute hydrochloric acid until the solution is faintly acid, followed by 10 cc. of N/2 hydrochloric acid and 10 cc. of 2.5% oxalic acid. Boil the solution until the precipitate becomes granular and add, with constant stirring, 15 cc. of a saturated solution of ammonium oxalate. Cool and add, with constant stirring, 8 cc. of 20% sodium acetate solution and allow to stand 4–18 hours. Filter and wash with hot water until free from chlorids. Dissolve the precipitate in hot, dilute sulphuric acid and titrate with N/10 potassium permanganate solution. (1 cc. N/10 $KMnO_4$=0.0028 gram CaO.)

If preferred the calcium oxalate precipitate may be ignited and weighed, correcting for occluded manganese.

---

[1] Presented by P. F. Trowbridge.
[2] *J. Biol. Chem.*, 1910, 7: 83.

MAGNESIUM.

To the filtrate and washings from the calcium determination add 25 cc. of strong nitric acid and evaporate to dryness. Take up with dilute hydrochloric acid and make to volume of about 100 cc. Add 5 cc. of sodium citrate (10% solution) and 10 cc. of sodium hydrogen phosphate solution or enough to precipitate all the magnesium. Add dilute ammonium hydroxid, with constant stirring, until the solution is faintly alkaline, then add about 25 cc. of strong ammonium hydroxid and leave in a cool place overnight. Filter and wash with 2.5% ammonium hydroxid solution. Dissolve the precipitate in dilute hydrochloric acid and reprecipitate as before. Allow to stand 2 or 3 hours, filter and wash with 2.5% ammonium hydroxid solution, ignite and weigh as magnesium pyrophosphate.

TABLE 1.

Calcium and magnesium.

CALCIUM OXID	MAGNESIUM OXID	REMARKS
per cent	*per cent*	
3.00	-----	Volumetric
3.04	-----	
3.04	-----	Volumetric
3.04	-----	1 gram of manganese sulphate added to solution before precipitating calcium
3.04	10.14	Gravimetric
3.12	10.10	Mangano-manganic oxid present, 0.24 per cent
3.04	-----	Gravimetric
3.12	-----	Mangano-manganic oxid present, 0.20 per cent
Average 3.055	10.12	
Theory 3.00	10.00	

FERRIC AND ALUMINIC OXIDS.

To the filtrate and washings from the magnesium determination, add 25 cc. of concentrated nitric acid and evaporate to dryness. Take up with dilute hydrochloric acid and dilute to about 150 cc. Make ammoniacal and allow to stand on the steam bath until the iron and aluminium have been precipitated as phosphates. Filter and wash with hot water until free from chlorids. Dissolve the precipitate on the filter with hot nitric acid (1 to 5), wash the filter thoroughly and precipitate as before. Filter, wash the precipitate with hot water until free from chlorids, ignite and weigh as ferric and aluminic oxids.

If it is desired to determine the ferric oxid separately, fuse the residue with about 4 grams of potassium bisulphate, cool, add 5 cc. of concentrated sulphuric acid and digest until all sulphate is dissolved to a clear solution. Reduce with zinc, cool, and titrate with N/50 potassium permanganate solution.

MANGANESE.

To 50 cc. of the solution, representing 0.5 gram of ash, add about 15 cc. of concentrated sulphuric acid and evaporate to expel hydrochloric acid. When the solution has reached a small volume add 5–10 cc. of nitric acid and continue the evaporation. It is not

necessary nor desirable to evaporate until *dense* fumes appear, since the ferric sulphate then dissolves with difficulty. Nitric acid may be present, but not hydrochloric. Add water, a little at a time, heat until the iron salts have dissolved and dilute to about 150 cc. Add about 0.3 gram of potassium periodate, heat just to boiling for a few minutes and allow to cool. The standard is prepared in the following manner: To a volume of water equal to the sample add 15 cc. of sulphuric acid and sufficient pure ferric nitrate, free from manganese, so that this solution will contain about the same amount of iron as the samples. Add standard permanganate solution, noting the amount, until the color is slightly darker than the sample, and then the same amount of periodate and boil as before. When cool, transfer the sample and standard to 250 cc. flasks and make to mark. If the color is weak it may be necessary to make to smaller volume. Compare the colors in any standard colorimeter.

TABLE 2.

Manganese.

SAMPLE	MANGANO-MANGANIC OXID
	per cent
1	0.211
2	0.211
3	0.208
4	0.220
Average	0.213
Theory	0.20

RECOMMENDATIONS.

It is recommended—

(1) That further study be made of the methods as outlined for calcium, magnesium, iron and aluminium with solutions approximating the composition of the ash from cereals.

(2) That further study be made of the colorimetric method for the determination of manganese.

REPORT ON INSECTICIDES.

By R. C. ROARK[1] (Bureau of Chemistry, Washington, D. C.), *Referee.*

The work included a study of methods for the determination of arsenic trioxid and arsenic pentoxid in the presence of each other in lead arsenate; for the determination of lead oxid, zinc oxid and copper in such preparations as Bordeaux-lead arsenate, Bordeaux-zinc arsenite, etc.; and for the analysis of lime-sulphur solution.

[1] Present address, General Chemical Co., Baltimore Works, Baltimore, Md.

LEAD ARSENATE WITH LEAD ARSENITE.

To test methods for the direct determination of trivalent and pentavalent arsenic in the presence of each other, a sample of lead arsenate with lead arsenite was prepared by thoroughly mixing 300 grams of dilead arsenate ($PbHAsO_4$) with 100 grams of lead arsenite. The lead arsenate was precipitated by the addition of a solution of lead nitrate to a solution of potassium dihydrogen arsenate (KH_2AsO_4), the latter being in slight excess. The lead arsenite was prepared by adding a solution of arsenic trioxid in water to a solution of lead acetate containing a little free acetic acid. The slight amount of precipitate that formed on standing overnight was filtered off, and ammonia added in excess to the filtrate, throwing down lead arsenite, $Pb_3(AsO_3)_2$. Both the lead arsenate and lead arsenite were thoroughly washed, dried, and put through a No. 40 sieve before mixing.

On analysis the lead arsenate was shown to have the theoretical composition for dilead arsenate (33.11 per cent of arsenic pentoxid), while the lead arsenite contained 21.04 per cent of arsenic trioxid and 0.14 per cent of arsenic pentoxid. The mixture of the two submitted for cooperative work should contain, therefore, 5.26 per cent of arsenic trioxid and 24.86 per cent of arsenic pentoxid, or a total of 30.97 per cent calculated as arsenic pentoxid.

The methods tested on this sample are as follows:

TOTAL ARSENIC TRIOXID.

Weigh an amount of the powdered sample equal to the amount of arsenic trioxid to which 1000 cc. of the iodin solution are equivalent. Transfer to a 200 cc. graduated flask, add 100 cc. of dilute sulphuric acid (water, 85 cc.; concentrated sulphuric acid, 15 cc.), and boil for 30 minutes. Cool, make to volume, shake thoroughly, filter through a dry filter, take 100 cc. of the filtrate and nearly neutralize with a strong solution of sodium hydroxid, using a few drops of phenolphthalein as indicator. If the neutral point is passed make acid again with dilute sulphuric acid, then add sodium bicarbonate in excess and titrate with N/20 iodin solution in the usual way. The number of cc. of iodin solution used in this titration multiplied by 0.2 equals the per cent of arsenic trioxid in the sample.

TOTAL ARSENIC PENTOXID.

REAGENTS.

Solutions required:

Starch solution.—Prepare as directed under Paris green[1].

Standard iodin solution.—Prepare as directed under Paris green, but calculate in terms of arsenic pentoxid.

Standard thiosulphate solution.—Prepare an approximately N/20 solution as follows:

Weigh 13 grams of crystallized C. P. sodium thiosulphate, dissolve in water which has been recently boiled and cooled, filter, and make to volume in a 1 liter graduated flask, using water that has been recently boiled and cooled. To standardize this solution, proceed as follows:

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 63.

(a) Dissolve about 0.7 gram of C. P. dilead arsenate ($PbHAsO_4$[1]) in 50 cc. of concentrated hydrochloric acid in an Erlenmeyer flask. If necessary to effect solution, heat on the steam bath, keeping the flask covered with a watch glass to prevent evaporation of the acid. Cool to 20–25°C., add 10 cc. of potassium iodid solution (20 grams of potassium iodid per 100 cc.), and 50 cc. (or more if necessary to produce a clear solution) of ammonium chlorid solution (25 grams of ammonium chlorid per 100 cc.) and immediately titrate the liberated iodin with the thiosulphate solution. When the color of the solution becomes a faint yellow, dilute with about 150 cc. of water[2] and continue the titration carefully, drop by drop, until the solution is colorless, using starch paste as an indicator near the end point. From the weight of lead hydrogen arsenate and the number of cc. of sodium thiosulphate solution used, calculate the value of the latter in terms of arsenic pentoxid. (As_2O_5 in $PbHAsO_4$ = 33.11 per cent.)

(b) Titrate 50 cc. of the standard iodin solution, diluted with about 100 cc. of water, with the thiosulphate solution, to a colorless solution, using starch paste as an indicator, and from the ratio of the two solutions, and the value of the iodin solution in terms of arsenic pentoxid, calculate the value of the thiosulphate solution in terms of arsenic pentoxid.

The values obtained by these two methods of standardization should check very closely. The value obtained by procedure (a) is to be preferred.

DETERMINATION.

Weigh an amount of the powdered sample equal to twice the amount of arsenic pentoxid to which 100 cc. of the thiosulphate solution are equivalent. Transfer to an Erlenmeyer flask, dissolve in 50 cc. of concentrated hydrochloric acid, and proceed as directed under standardization (a). The number of cc. of thiosulphate solution used in the titration, divided by 2, represents directly the per cent of arsenic pentoxid in the sample.

The following results on this sample have been received:

---

[1] Pure dilead arsenate may be prepared by pouring a solution of lead nitrate into a solution of potassium dihydrogen arsenate (KH_2AsO_4), which should be in excess. The precipitate should be collected by filtration, dissolved in the smallest possible quantity of boiling nitric acid (1 to 4), and this solution then poured into a large quantity of distilled water. The precipitate which results should be collected and dried at 110°C.

[2] Later results indicate that dilution is unnecessary. It is very important to standardize and analyze under the same conditions, especially concentration of acid.

Determination of arsenic trioxid and arsenic pentoxid in mixtures of lead arsenate and lead arsenite.

ANALYST	ARSENIC TRIOXID (As_2O_3)	ARSENIC PENTOXID (As_2O_5)	TOTAL ARSENIC CALCULATED AS As_2O_5	TOTAL ARSENIC BY DISTILLATION, CALCULATED AS As_2O_5
	per cent	*per cent*	*per cent*	*per cent*
J. J. T. Graham, Bureau of Chemistry, Washington, D. C.	4.92	25.33	----	30.95
	4.87	25.30	----	31.00
	4.85	25.20	----	----
	4.82	----	----	----
	4.90	----	----	----
Average	4.87	25.28	30.94	30.98
A. J. Flume, Agricultural Experiment Station, Geneva, N. Y.	4.68[a]	25.69[a]	----	----
	4.60[a]	25.74[a]	----	30.10
	4.75[b]	26.10[b]	----	----
	4.67[b]	26.15[b]	----	30.53
	4.64[c]	25.51[c]	----	----
	4.58[c]	25.56[c]	----	29.89
Average	4.65	25.79	31.19	30.17
H. L. Fulmer, Ontario Agricultural College, Guelph, Canada.	5.12	25.7	31.65	----
D. K. French, Dearborn Chemical Co., Chicago, Ill.	5.52	24.81	----	31.24
	5.52	24.85	----	31.25
	5.51	24.79	----	31.27
Average	5.52	24.82	31.24	31.25
R. C. Roark, Bureau of Chemistry, Washington, D. C.	5.32	25.10	----	31.26
	5.26	25.10	----	----
Average	5.29	25.10	31.25	31.26
R. N. Miller, Bureau of Chemistry, Washington, D. C.	5.32	25.10	----	31.28
	5.24	25.15	----	31.13
	5.28	----	----	----
Average	5.28	25.13	31.26	31.21
W. W. Webber, Agricultural Experiment Station, Orono, Me.	4.82	25.76	----	----
	4.88	25.60	----	----
Average	4.85	25.68	31.31	----
General average	5.00	25.40	31.21	30.90
Calculated value	5.26	24.86	30.97	30.97

[a] Standardized with arsenic trioxid.
[b] Standardized with dilead arsenate.
[c] Standardized with potassium iodate.

COMMENTS BY ANALYST.

A. J. Flume.—The thiosulphate solution was standardized by means of dilead arsenate and potassium iodate. A ratio was established with the iodin solution, and the arsenic equivalent of both solutions was determined. The iodin solution was standardized with arsenic trioxid, and from the ratio above the arsenic equivalent of the thiosulphate was calculated.

DISCUSSION.

There is quite a variation in the results for both arsenic trioxid and arsenic pentoxid as determined by the different analysts. This is no doubt due to incomplete mixture of the sample before weighing out portions for analysis. The lead arsenate was a very fine, light and fluffy powder, while the lead arsenite was dense and in the form of much coarser particles, which had a tendency to separate on agitation. The referee found it necessary to mix thoroughly each sample in order to get duplicate portions from the same bottle to agree.

The fact that for each analyst the sum of the arsenic trioxid and arsenic pentoxid, calculated to a common basis, agrees with the total arsenic determined by the distillation method, shows that the methods for these determinations are accurate.

The referee presents in a separate paper, pp. 365—7, the results of analysis of a number of commercial lead arsenates by the above method for arsenic trioxid and a slight modification of the method for arsenic pentoxid, showing that these methods yield accurate results on commercial samples.

The fact that one of the analysts obtained low results for total arsenic by the distillation method may be accounted for by the presence of a large amount of cupric chlorid in the cuprous chlorid used. Samples of so-called cuprous chlorid were found sometimes to consist almost entirely of cupric chlorid[1].

BORDEAUX-LEAD ARSENATE AND BORDEAUX-ZINC ARSENITE.

For testing the methods for lead oxid, copper and zinc oxid, two samples were prepared: No. 1, Bordeaux-lead arsenate; No. 2, Bordeaux zinc arsenite.

The Bordeaux-lead arsenate was prepared by mixing 280 grams of dilead arsenate, made as previously described but recrystallized from nitric acid, with 140 grams of dry Bordeaux mixture, made from C. P. materials. This Bordeaux, when analyzed by the official electrolytic method, showed a copper content of 18.45 per cent, and the lead arsenate yielded theoretical results for lead oxid in dilead arsenate, namely, 64.29 per cent. The Bordeaux-lead arsenate should, therefore, contain 21.43 per cent of lead oxid and 12.08 per cent of copper.

[1] A solution of cuprous chlorid may be prepared by dissolving cupric chlorid in hydrochloric acid (sp. gr. 1.19), adding several strips of copper foil and enough water to prevent loss of hydrochloric acid when the solution is boiled, and heating for an hour. An excess of metallic copper must always be present. The solution is then poured into about twice its volume of water, the cuprous chlorid which precipitates is collected on a Büchner filter, washed quickly with alcohol, dried at 110°C., powdered and preserved in a glass-stoppered bottle in the dark. By removing the water from the cuprous chlorid with alcohol, no oxidation occurs on drying.

Copper oxid or copper carbonate may be used instead of cupric chlorid for preparing cuprous chlorid in the above manner.

The filtrate from the precipitated cuprous chlorid still contains a considerable amount of this salt. It may be concentrated by evaporation in the presence of metallic copper and more cuprous chlorid obtained as before.

In preparing the Bordeaux-zinc arsenite, 200 grams of the above Bordeaux were mixed with 200 grams of zinc meta-arsenite, $ZnAs_2O_4$. This latter was prepared according to the method of Avery[1] by adding a solution of arsenic trioxid to a solution of zinc chlorid, both solutions being slightly acid, and then adding sodium hydroxid solution to neutrality. A determination of zinc in this sample of zinc meta-arsenite by the method of Balls and McDonnell[2] yielded 23.45 per cent of zinc, equivalent to 29.19 per cent of zinc oxid (theory 29.13 per cent).

The Bordeaux-zinc arsenite should contain, therefore, 14.57 per cent of zinc oxid and 9.24 per cent of copper.

The directions that were sent out for the determination of these constituents are as follows:

GENERAL PROCEDURE FOR THE ANALYSIS OF A PRODUCT CONTAINING ARSENIC, ANTIMONY, LEAD, COPPER, ZINC, IRON, CALCIUM, MAGNESIUM, ETC.

(Applicable to such preparations as Bordeaux-lead arsenate; Bordeaux-zinc arsenite; Bordeaux-Paris green; Bordeaux-calcium arsenate, etc.).

Lead oxid (PbO).—Weigh 1 gram of the dry powdered sample, transfer to a beaker, add 5 cc. of hydrobromic acid (sp. gr. 1.31) and 15 cc. of hydrochloric acid (sp. gr. 1.19) and evaporate to dryness to remove arsenic; repeat this treatment; then add 20 cc. of hydrochloric acid (sp. gr. 1.19) and again evaporate to dryness. Dissolve in 25 cc. of 2N hydrochloric acid, dilute to 100 cc. and pass in hydrogen sulphid until precipitation is complete. Filter, and wash precipitate thoroughly with N/2 hydrochloric acid, saturated with hydrogen sulphid. Save the filtrate and washings for the determination of zinc. (If antimony is present it should be removed by digesting the sulphids with sodium sulphid. However, antimony is only occasionally present and always in small amount and usually only in samples containing zinc, so that in general this step may be omitted.) Transfer the filter paper containing the sulphids of lead and copper to a porcelain casserole or evaporating dish and completely oxidize all organic matter by heating with a few cc. of concentrated sulphuric acid, together with a little fuming nitric acid; then completely remove all nitric acid by heating on the hot plate with sulphuric acid to copious evolution of white fumes, cool, and determine lead as the sulphate as directed for lead arsenate[3]. From the weight of lead sulphate calculate the amount of lead oxid present, using the factor: $PbSO_4 \times 0.73600 = PbO$.

Copper.—Evaporate the filtrate and washings from the lead sulphate precipitate, remove excess of sulphuric acid by fuming on the hot plate, and determine copper as directed under Bordeaux mixture, either by the electrolytic or Low's titration method[4].

Zinc.—Evaporate the filtrate and washings from the precipitate of copper and lead sulphids to a small volume, add 1 or 2 cc. of concentrated nitric acid, boil for a few minutes, then evaporate to dryness, add a few cc. of concentrated sulphuric acid and heat to fuming, dissolve in a little water, neutralize with concentrated potassium hydroxid solution, using phenolphthalein solution as indicator, and then add not over 10 grams excess solid potassium hydroxid. Transfer to a weighed nickel crucible and electrolyze, using a rotating anode and a current of about 3.5 amperes. When deposition is complete, which should take about 1 hour, wash with water by siphoning, then

[1] *J. Am. Chem. Soc.*, 1906, **28**: 1163.
[2] *J. Ind. Eng. Chem.*, 1915, **7**: 26.
[3] *Assoc. Official Agr. Chemists, Methods*, 1916, 68.
[4] *Ibid.*, 70.

rinse with alcohol, dry for a minute or so in an oven, and weigh as metallic zinc. Calculate zinc oxid, using the factor: $Zn \times 1.24476 = ZnO$.

Results on the samples of Bordeaux-lead arsenate and Bordeaux-zinc arsenite received are as follows:

Cooperative results.

ANALYST	BORDEAUX-LEAD ARSENATE		BORDEAUX-ZINC ARSENITE	
	Lead oxid (PbO)	Copper (Cu)	Zinc oxid (ZnO)	Copper (Cu)
	per cent	*per cent*	*per cent*	*per cent*
O. D. Knight, Bureau of Chemistry, Washington, D. C.	21.27	12.08	13.49	9.33
	21.27	12.10	13.53	9.33
Average	21.27	12.09	13.51	9.33
J. J. T. Graham	21.37	12.32	12.12	9.26
	21.27	12.26	12.32	9.34
	21.37	12.30	----	9.23
	21.31	12.14	----	9.28
Average	21.33	12.26	12.22	9.28
A. J. Flume	19.74	11.42	----	----
	19.52	11.48	----	----
	19.52	----	----	----
Average	19.59	11.45	----	----
D. K. French	21.26	13.18	----	9.78
	21.20	13.20	----	9.75
	21.19	13.03	----	9.86
Average	21.22	13.14	----	9.80
R. N. Miller	21.22	12.28	13.17	9.34
	21.52	12.24	14.09	9.38
	----	----	11.30	----
Average	21.37	12.26	12.85	9.36
R. C. Roark	21.20	11.71	13.36	9.14
	21.27	11.60	13.82	9.24
	21.68	----	----	----
	21.23	11.64	----	----
Average	21.35	11.65	13.59	9.19
W. W. Webber	20.78	12.30	----	9.91[a]
	20.74	12.30	----	9.86[b]
Average	20.76	12.30	----	9.89
N. H. Borden, Bureau of Chemistry, Washington, D. C.	21.37	12.37	13.98	9.28
	21.36	12.39	13.98	9.28
Average	21.37	12.38	13.98	9.28
General Average	21.03	12.22	13.20	9.45
Calculated value	21.43	12.08	14.57	9.24

[a] Low's titration method.
[b] Electrolytic method.

COMMENTS BY ANALYSTS.

J. J. T. Graham.—In the method for lead oxid in Bordeaux-lead arsenate it is suggested that the referee's instructions be amended to eliminate any silica that may be present, as this may cause an error.

N. H. Borden.—In the electrolytic determination of zinc 14.17 per cent of zinc oxid was obtained, using 10 grams excess of sodium hydroxid instead of potassium hydroxid. In all cases the electrolysis was continued about 75 minutes.

DISCUSSION.

The method of getting rid of arsenic by reduction to As^{III} with hydrobromic acid and volatilization of the trichlorid by evaporation of the hydrochloric acid solution to complete dryness works very satisfactorily. The precipitation of the sulphids of lead and copper is accompanied with certain difficulties. If the solution is too acid the precipitation of lead is not complete; if not sufficiently acid, some zinc sulphid is brought down. The results for lead oxid obtained by the analysts are good, being low in one instance; the results for copper are only fair; and the results for zinc oxid are quite poor. It is recommended that more work be done on these or other methods for the determination of these substances before adoption by the association.

LIME-SULPHUR SOLUTION.

To test the method for lime-sulphur solution, three samples were sent out.

Sample 1 was prepared by passing hydrogen sulphid into a mixture of C. P. calcium hydroxid and water for several days, boiling this solution of calcium hydrosulphid (together with a slight excess of calcium hydroxid remaining unacted upon) with an excess of sulphur in a large flask provided with a reflux condenser, a stream of hydrogen sulphid being passed during the operation. When the reaction had proceeded to apparent completion the solution was filtered hot, allowed to cool in the absence of air and bottled.

Sample 2 was prepared by mixing 1100.5 grams of Sample 1 with 999.0 grams of a solution of sodium thiosulphate prepared by dissolving 400 grams of C. A. F. Kahlbaum's sodium thiosulphate in water and making the solution up to 1000 cc. Analysis of this solution of sodium thiosulphate showed thiosulphate sulphur by titration with iodin solution equivalent to 8.61 per cent. Sample 2 should contain, therefore, 4.097 per cent of thiosulphate sulphur plus 0.52 times the thiosulphate sulphur in Sample 1. It is extremely unlikely, considering the method of preparation, that Sample 1 contains as much as 0.10 per cent of thiosulphate sulphur, and certainly not more than this amount. Assuming 0.10 per cent of thiosulphate sulphur for Sample 1, Sample 2 should contain 4.15 per cent of thiosulphate sulphur.

Sample 3 is a commercial concentrated lime-sulphur solution.

The following directions were sent out:

PREPARATION OF SAMPLE.

Proceed as directed in the *Association of Official Agricultural Chemists, Methods*, 1916, 76.

TOTAL SULPHUR.

Proceed as directed in the *Association of Official Agricultural Chemists, Methods*, 1916, 76.

I. Zinc Chlorid Method.

SULPHID SULPHUR.

Pipette 10 cc. of the solution prepared for analysis into a beaker, and immediately add a slight excess of ammoniacal zinc solution (prepared by dissolving 50 grams of pure zinc chlorid in water, adding ammonia in sufficient quantity to redissolve the precipitate first formed, and then adding 50 grams of ammonium chlorid[1] and diluting to 1 liter). Stir thoroughly so as to assure complete precipitation of the sulphid sulphur, filter, and wash 4 or 5 times with hot water. Transfer the filter paper containing the zinc sulphid to the beaker in which the precipitation was made, cover with a little water, disintegrate with a glass rod, and add about 3 grams of sodium peroxid, keeping the beaker well covered with a watch glass. Warm on the steam bath with frequent shaking until all the sulphid is oxidized to sulphate, adding more sodium peroxid if necessary. Make slightly acid with hydrochloric acid, filter to remove shreds of filter paper, wash thoroughly with hot water, and determine sulphur in the filtrate exactly as directed under "total sulphur".

THIOSULPHATE SULPHUR.

Proceed as directed in the *Association of Official Agricultural Chemists, Methods*, 1916, 76. Use very little starch paste in the titration so as not to interfere with the precipitation of sulphate sulphur with barium chlorid.

SULPHATE SULPHUR.

Proceed as directed in the *Association of Official Agricultural Chemists, Methods*, 1916, 77.

II. Cadmium Chlorid Method.

Proceed as directed in the zinc chlorid method, substituting for the ammoniacal solution of zinc chlorid an ammoniacal solution of cadmium chlorid prepared as follows:[2] Dissolve 50 grams of cadmium chlorid in water, add 400 cc. of ammonia (sp. gr. 0.90) and dilute to 1000 cc.

III. Iodin Titration Method.

For preparation of sample for analysis, determination of monosulphur equivalent and thiosulphate sulphur by methods "A", "B", "C", and "D"[3], use N/20 iodin solution standardized against pure arsenic trioxid and calculate results as follows:

$As_2O_3 \times 1.29588$ = thiosulphate sulphur (S).

$As_2O_3 \times 0.32397$ = monosulphur equivalent sulphur (S).

TOTAL LIME.

Proceed as directed in the *Association of Official Agricultural Chemists, Methods*, 1916, 77. Observe the precautions about solubility of calcium oxalate in hot water and directions for ignition given by Hillebrand.[4]

Results received are as follows:

[1] *J. Soc. Chem. Ind.*, 1912, **31**: 369.
[2] Thompson and Whittier. Del. Agr. Expt. Sta. Bull. **105**: 7.
[3] *J. Ind. Eng. Chem.*, 1916, 8: 624.
[4] U. S. Geol. Surv. Bull. 422: 119.

Cooperative results on

ANALYST	TOTAL SULPHUR	SULPHID SULPHUR			THIOSULPHATE SULPHUR		
		Zinc chlorid	Cadmium chlorid	Iodin	Zinc chlorid	Cadmium chlorid	"A"
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
J. J. T. Graham	9.44	9.36	9.43	9.05	0.07	0.04	0.15
	9.43	9.39	9.32	9.06	0.07	0.04	0.17
	9.43	----	----	----	0.06	----	----
	----	----	----	----	0.06	----	----
Average	9.43	9.38	9.38	9.06	0.07	0.04	0.16
F. C. Cook, Bureau of Chemistry, Washington, D. C.	9.17	8.96	----	----	0.14	----	0.60
	9.16	8.87	----	----	0.14	----	0.62
	----	----	----	----	----	----	0.64
Average	9.17	8.92	----	----	0.14	----	0.62
S. D. Averitt, Agricultural Experiment Station, Lexington, Ky.	8.90	----	----	8.68[a]	0.10	----	0.38
	----	----	----	8.70[a]	0.10	----	0.37
	----	----	----	8.70[a]	0.09	----	0.38
	8.92	----	----	----	0.10	----	0.37
Average	8.91	----	----	8.69	0.10	----	0.38
D. K. French	9.35	8.85	8.75	8.45	0.11	0.16	0.22
	9.23	8.72	8.69	----	0.12	0.12	0.19
	9.35	----	----	----	0.10	----	0.18
	9.29	----	----	----	----	----	----
Average	9.31	8.79	8.72	8.45	0.11	0.14	0.20
R. M. Chapin, Bureau of Animal Industry, Washington, D. C.	9.14	----	----	----	0.03	0.04	0.30
	9.12	----	----	----	0.04	----	0.26
Average	9.13	----	----	----	0.04	0.04	0.28
C. H. Robinson, Experimental Farm, Ottawa, Canada.	9.02	8.78	9.01	8.69	0.17	----	0.34
	9.02	8.80	8.98	8.71	0.17	----	0.31
Average	9.02	8.79	9.00	8.70	0.17	----	0.33
O. B. Winter, Agricultural Experiment Station, E. Lansing, Mich.	----	----	----	----	0.21	0.28	0.17
	----	----	----	----	0.21	0.26	0.21
	----	----	----	----	0.14	----	0.21
	----	----	----	----	0.13	----	0.26
	----	----	----	----	0.13	----	0.26
	----	----	----	----	0.13	----	0.20
	----	----	----	----	----	----	0.20
	----	----	----	----	----	----	0.14
	----	----	----	----	----	----	0.35
Average	----	----	----	----	0.16	0.27	0.22

[a] Weighed as sulphur.

lime-sulphur Solution 1.

THIOSULPHATE SULPHUR			SULPHATE SULPHUR			MONO-SULPHUR EQUIVALENT	CALCIUM OXID (CaO)
"B"	"C"	"D"	Zinc chlorid	Cadmium chlorid	Iodin		
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*
0.08	0.11	0.15	0.01	0.02	----	1.82	3.39
0.08	0.11	0.17	0.01	----	----	1.81	3.43
----	0.11	----	0.02	----	----	----	----
----	0.08	----	0.02	----	----	----	----
0.08	0.10	0.16	0.02	0.02	----	1.82	3.41
----	----	----	----	----	----	1.65	3.47
----	----	----	----	----	----	1.66	3.47
----	----	----	----	----	----	1.67	----
----	----	----	----	----	----	1.66	3.47
0.20	0.20	0.23	----	----	----	1.75	3.40
0.20	0.20	----	----	----	----	1.72	----
0.20	----	----	----	----	----	1.73	3.40
0.23	----	----	----	----	----	1.73	3.41
0.21	0.20	0.23	----	----	----	1.73	3.41
----	----	----	0.02	0.02	----	1.79	3.44
----	----	----	0.02	0.03	----	1.84	3.43
----	----	----	0.02	0.02	----	1.82	3.39
----	----	----	----	----	----	1.85	----
----	----	----	0.02	0.02	----	1.83	3.42
----	----	0.10	----	----	----	1.85	----
----	----	0.08	----	----	----	1.86	----
----	----	0.09	----	----	----	1.86	----
0.26	----	----	0.02	0.02	0.02	1.86	3.50
0.29	----	----	0.02	0.01	0.02	1.88	3.49
0.28	----	----	0.02	0.02	0.02	1.87	3.50
----	----	----	----	----	----	1.83	----
----	----	----	----	----	----	1.83	----
----	----	----	----	----	----	1.83	----
----	----	----	----	----	----	1.84	----
----	----	----	----	----	----	1.82	----
----	----	----	----	----	----	1.78	----
----	----	----	----	----	----	1.83	----
----	----	----	----	----	----	1.81	----
----	----	----	----	----	----	1.81	----
----	----	----	----	----	----	1.82	----

Cooperative results on

ANALYST	TOTAL SULPHUR	SULPHID SULPHUR			THIOSULPHATE SULPHUR		
		Zinc chlorid	Cadmium chlorid	Iodin	Zinc chlorid	Cadmium chlorid	"A"
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
R. N. Miller	9.09	8.56	8.67	4.92	0.10	0.06	0.56
	9.10	8.56	8.51	6.12	0.11	0.06	0.66
	----	----	8.84	4.88	----	----	0.79
	----	----	8.65	6.91	----	----	0.54
	----	----	8.79	----	----	----	0.54
	----	----	----	----	----	----	0.48
	----	----	----	----	----	----	0.38
	----	----	----	----	----	----	0.43
	----	----	----	----	----	----	0.41
	----	----	----	----	----	----	0.31
	----	----	----	----	----	----	0.28
	----	----	----	----	----	----	0.31
Average	9.10	8.56	8.69	5.71	0.11	0.06	0.47
W. W. Webber	8.55	6.24	8.49	8.51	0.22	0.22	0.82
	8.71	6.40	7.41	8.85	0.31	0.22	0.82
	8.85	----	----	----	----	----	----
	8.50	----	----	----	----	----	----
	8.60	----	----	----	----	----	----
Average	8.64	6.32	7.95	8.68	0.27	0.22	0.82
R. C. Roark	9.31	8.64	----	----	0.08	----	0.34
	9.24	8.70	----	----	0.10	----	0.29
Average	9.28	8.67	----	----	0.09	----	0.32
General average	9.08	8.49	8.73	7.88	0.13	0.14	0.38

Cooperative results on

ANALYST	TOTAL SULPHUR	SULPHID SULPHUR			THIOSULPHATE SULPHUR		
		Zinc chlorid	Cadmium chlorid	Iodin	Zinc chlorid	Cadmium chlorid	"A"
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
J. J. T. Graham	9.27	4.85	5.06	4.83	4.07	3.80	4.08
	9.24	4.81	5.14	4.99	4.07	3.82	4.21
	----	----	----	4.80	----	----	4.12
	----	----	----	----	----	----	4.33
	----	----	----	----	----	----	4.25
	----	----	----	----	----	----	3.91
	----	----	----	----	----	----	----
	----	----	----	----	----	----	----
Average	9.26	4.83	5.10	4.87	4.07	3.81	4.15

lime-sulphur Solution 1.—Concluded.

THIOSULPHATE SULPHUR			SULPHATE SULPHUR			MONO-SULPHUR EQUIVALENT	CALCIUM OXID (CaO)
"B"	"C"	"D"	Zinc chlorid	Cadmium chlorid	Iodin		
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*
----	----	0.25	trace	trace	0.29	1.67	3.41
----	----	0.18	----	----	0.37	1.61	3.37
----	----	0.20	----	----	0.36	1.51	----
----	----	0.18	----	----	0.35	1.67	----
----	----	0.15	----	----	----	1.63	----
----	----	----	----	----	----	1.69	----
----	----	----	----	----	----	1.75	----
----	----	----	----	----	----	1.72	----
----	----	----	----	----	----	1.75	----
----	----	----	----	----	----	1.76	----
----	----	----	----	----	----	1.78	----
----	----	----	----	----	----	1.76	----
----	----	0.19	trace	trace	0.34	1.69	3.39
----	----	----	0.05	0.02	----	1.35	3.52
----	----	----	0.06	0.03	----	1.35	3.54
----	----	----	----	----	----	----	----
----	----	----	----	----	----	----	----
----	----	----	----	----	----	----	----
----	----	----	0.06	0.03	----	1.35	3.53
----	----	----	----	----	----	1.72	3.41
----	----	----	----	----	----	1.75	----
----	----	----	----	----	----	1.74	3.41
0.18	0.12	0.17	0.02	0.02	0.23	1.74	3.44

lime-sulphur Solution 2.

THIOSULPHATE SULPHUR			SULPHATE SULPHUR			MONO-SULPHUR EQUIVALENT	CALCIUM OXID (CaO)
"B"	"C"	"D"	Zinc chlorid	Cadmium chlorid	Iodin		
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*
4.21	4.10	3.91	0.02	0.02	0.14	0.97	1.84
4.19	4.04	3.93	0.02	0.02	0.14	0.94	1.97
4.19	3.43	----	----	----	0.31	0.97	----
----	3.56	----	----	----	0.36	0.89	----
----	3.58	----	----	----	0.36	0.93	----
----	3.32	----	----	----	0.25	1.02	----
----	3.91	----	----	----	----	----	----
----	4.19	----	----	----	----	----	----
4.20	3.77	3.92	0.02	0.02	0.26	0.95	1.91

Cooperative results on

ANALYST	TOTAL SULPHUR	SULPHID SULPHUR			THIOSULPHATE SULPHUR		
		Zinc chlorid	Cadmium chlorid	Iodin	Zinc chlorid	Cad. mium chlorid	"A"
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
R. M. Chapin	----	----	----	----	4.11	3.82	4.17
	----	----	----	----	4.06	----	----
Average	----	----	----	----	4.09	3.82	4.17
D. K. French	8.99	4.19	3.88	3.36	4.18	4.26	4.23
	9.07	4.17	----	----	4.22	4.27	4.18
	9.12	4.01	----	----	4.18	4.29	4.04
	----	----	----	----	----	----	----
Average	9.06	4.12	3.88	3.36	4.19	4.27	4.15
C. H. Robinson	8.94	4.63	4.86	4.65	4.28	4.05	4.29
	8.98	4.56	4.80	4.66	4.26	4.07	4.29
	----	----	----	----	----	----	----
	----	----	----	----	----	----	----
Average	8.96	4.60	4.84	4.66	4.27	4.06	4.29
O. B. Winter	----	----	----	----	4.24	4.22	4.22
	----	----	----	----	4.22	4.20	4.21
	----	----	----	----	4.21	----	4.16
	----	----	----	----	4.22	----	4.19
Average	----	----	----	----	4.22	4.21	4.20
R. N. Miller	8.94	5.18	4.97	3.97	4.24	----	4.43
	8.93	5.10	4.97	4.43	4.25	----	4.59
	----	5.07	----	----	----	----	4.78
	----	----	----	----	----	----	4.81
	----	----	----	----	----	----	4.83
Average	8.94	5.12	4.97	4.20	4.25	----	4.69
W. W. Webber	8.93	3.46	4.65	5.97	4.13	3.91	4.40
	8.90	3.27	4.99	5.46	4.10	3.89	4.53
Average	8.92	3.37	4.82	5.72	4.12	3.90	4.47
F. C. Cook	8.91	4.66	----	----	4.11	----	4.63
	8.94	4.62	----	----	4.16	----	4.73
	----	4.59	----	----	4.13	----	----
Average	8.93	4.62	----	----	4.13	----	4.68
S. D. Averitt	----	----	----	4.60[a]	4.19	----	4.20
	----	----	----	4.62[a]	4.17	----	4.22
Average	----	----	----	4.61	4.18	----	4.21
R. C. Roark	9.10	4.63	----	----	4.09	----	4.22
	----	4.76	----	----	4.09	----	4.22
Average	9.10	4.70	----	----	4.09	----	4.22
General average	9.02	4.50	4.81	4.70	4.17	4.05	4.33

[a] Weighed as sulphur.

lime-sulphur Solution 2.—Concluded.

THIOSULPHATE SULPHUR			SULPHATE SULPHUR			MONO-SULPHUR EQUIVALENT	CALCIUM OXID (CaO)
"B"	"C"	"D"	Zinc chlorid	Cadmium chlorid	Iodin		
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*
----	----	3.88	----	----	----	1.00	----
----	----	----	----	----	----	----	----
----	----	3.88	----	----	----	1.00	----
----	----	----	0.02	0.02	----	0.99	1.83
----	----	----	0.03	0.03	----	1.06	1.84
----	----	----	0.03	0.03	----	1.02	1.83
----	----	----	----	----	----	----	1.84
----	----	----	0.03	0.03	----	1.02	1.84
4.29	----	----	0.05	0.05	0.06	1.02	1.78
4.28	----	----	0.05	0.04	0.06	1.02	1.82
----	----	----	----	----	----	----	1.88[a]
----	----	----	----	----	----	----	1.88[a]
4.29	----	----	0.05	0.05	0.06	1.02	1.84
----	----	----	----	----	----	0.96	----
----	----	----	----	----	----	0.95	----
----	----	----	----	----	----	0.96	----
----	----	----	----	----	----	0.96	----
----	----	----	----	----	----	0.96	----
----	----	----	----	----	0.01	0.93	2.21
----	----	----	----	----	0.01	0.90	2.24
----	----	----	----	----	----	0.88	----
----	----	----	----	----	----	0.89	----
----	----	----	----	----	----	0.89	----
----	----	----	----	----	0.01	0.90	2.23
----	----	----	0.03	----	----	0.81	1.77
----	----	----	0.02	----	----	0.82	1.81
----	----	----	0.03	----	----	0.82	1.79
----	----	----	----	----	----	0.82	1.76
----	----	----	----	----	----	0.79	1.79
----	----	----	----	----	----	0.79	1.83
----	----	----	----	----	----	0.80	1.79
4.20	----	----	----	----	----	0.98	1.78
4.23	----	----	----	----	----	0.97	----
4.22	----	----	----	----	----	0.98	1.78
----	----	----	----	----	----	0.92	1.80
----	----	----	----	----	----	0.94	1.79
----	----	----	----	----	----	0.93	1.80
4.23	3.77	3.91	0.03	0.03	0.17	0.93	1.86

[a] Weighed as sulphur.

Cooperative results on

ANALYST	TOTAL SULPHUR	SULPHID SULPHUR			THIOSULPHATE SULPHUR		
		Zinc chlorid	Cadmium chlorid	Iodin	Zinc chlorid	Cadmium chlorid	"A"
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
R. M. Chapin	23.75	----	----	----	0.72	----	0.98
	23.74	----	----	----	0.74	----	0.98
Average	23.75	----	----	----	0.73	----	0.98
J. J. T. Graham	23.78	22.50	----	22.25	0.99	----	0.98
	23.70	22.26	----	21.25	0.92	----	0.82
Average	23.74	22.38	----	21.75	0.96	----	0.90
D. K. French	22.73	22.51	22.73	22.60	0.88	0.88	0.98
	22.81	22.14	----	22.64	0.93	0.89	0.94
	----	----	----	22.65	----	----	----
Average	22.77	22.33	22.73	22.63	0.91	0.89	0.96
C. H. Robinson	23.90	22.62	23.21	22.80	0.85	0.30	0.82
	23.97	22.70	23.28	22.75	0.86	0.30	0.83
Average	23.94	22.66	23.25	22.78	0.86	0.30	0.83
O. B. Winter	----	----	----	----	0.92	0.85	0.92
	----	----	----	----	0.95	0.88	0.92
	----	----	----	----	----	----	0.95
	----	----	----	----	----	----	0.92
	----	----	----	----	----	----	0.92
Average	----	----	----	----	0.94	0.87	0.93
R. N. Miller	23.78	23.32	23.64	----	0.74	----	1.42
	23.82	23.45	23.15	----	0.77	----	1.37
	----	----	----	----	----	----	1.33
	----	----	----	----	----	----	----
Average	23.80	23.39	23.40	----	0.76	----	1.36
W. W. Webber	23.89	21.51	22.86	----	0.74	0.48	0.60
	24.38	21.67	21.98	----	0.76	0.51	0.63
	24.99	----	----	----	----	----	----
	25.44	----	----	----	----	----	----
	23.48	----	----	----	----	----	----
Average	24.44	21.59	22.42	----	0.75	0.50	0.62
R. C. Roark	24.13	22.36	----	----	0.67	----	1.18
	23.83	----	----	----	0.68	----	1.09
Average	23.98	22.36	----	----	0.68	----	1.14
General average	23.89	22.46	22.98	22.42	0.82	0.64	0.98

lime-sulphur Solution 3.

THIOSULPHATE SULPHUR			SULPHATE SULPHUR			MONO-SULPHUR EQUIVALENT	CALCIUM OXID (CaO)
"B"	"C"	"D"	Zinc chlorid	Cadmium chlorid	Iodin		
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*
----	----	----	----	----	----	4.72	----
----	----	----	----	----	----	4.69	----
----	----	----	----	----	----	4.71	----
----	----	----	----	----	----	4.60	9.73
----	----	----	----	----	----	4.63	9.48
----	----	----	----	----	----	4.62	9.61
----	----	----	0.06	0.06	----	4.54	9.19
----	----	----	0.06	0.06	----	4.59	9.21
----	----	----	----	----	----	----	----
----	----	----	0.06	0.06	----	4.57	9.20
0.83	----	----	0.08	0.08	0.11	4.72	9.17
0.84	----	----	0.09	0.07	0.12	4.71	9.17
0.84	----	----	0.09	0.08	0.12	4.72	9.17
----	----	----	----	----	----	4.67	----
----	----	----	----	----	----	4.67	----
----	----	----	----	----	----	4.68	----
----	----	----	----	----	----	4.66	----
----	----	----	----	----	----	4.67	----
----	----	----	----	----	----	4.67	----
----	----	----	----	----	0.01	4.81	9.27
----	----	----	----	----	0.01	4.85	9.33
----	----	----	----	----	----	4.81	----
----	----	----	----	----	----	4.79	----
----	----	----	----	----	0.01	4.82	9.30
----	----	----	0.01	0.03	----	4.20	9.54
----	----	----	0.02	0.02	----	4.26	9.44
----	----	----	----	----	----	----	----
----	----	----	----	----	----	----	----
----	----	----	----	----	----	----	----
----	----	----	0.02	0.03	----	4.23	9.49
----	----	----	----	----	----	4.53	9.19
----	----	----	----	----	----	4.55	----
----	----	----	----	----	----	4.54	9.19
0.84	----	----	0.05	0.05	0.06	4.64	9.34

Mr. R. M. Chapin of the Bureau of Animal Industry, sent in the following results on these solutions when analyzed according to his methods[1]. These methods appear to be desirable in many ways, and the referee regrets that they were not more extensively tested by the members of the association this year.

Analyses of association lime-sulphur samples according to Chapin's methods.

DETERMINATION	SOLUTION 1	SOLUTION 2	SOLUTION 3
	per cent	*per cent*	*per cent*
Hydrogen sulphid sulphur (reaction figure)	0.12	0.05	0.06
	0.12	0.05	0.06
Polysulphid sulphur	7.12	3.66	18.28
	7.15	3.68	18.34
Thiosulphate sulphur	0.09	4.20	0.84
	0.09	4.20	0.85
Sulphid acid figure (monosulphid sulphur)	2.00	1.04	4.82
	2.00	1.04	4.81
Sulphid sulphur (sum of monosulphid and polysulphid sulphur)	9.14	4.71	23.13

COMMENTS BY ANALYSTS ON LIME-SULPHUR METHODS.

S. D. Averitt.—The methods as given this year for total sulphur and total lime required too much manipulation and time for this character of work. Moreover, figures for total sulphur and lime by these methods are practically identical with those obtained by shorter methods recommended in 1913.

DETERMINATION	1916 INSTRUCTIONS	1913 INSTRUCTIONS
Total sulphur	8.90	8.88
	8.92	8.89
Total lime (CaO)	3.41	3.39
	3.40	3.38

It is impossible to explain the high figures for thiosulphate in Sample 1 by the iodin titration method unless it was made by diluting a lime-sulphur solution with lime water.

The low figures for thiosulphate in this sample by the zinc chlorid method are due to adsorption of thiosulphate by the precipitated zinc sulphid.

In Sample 2, containing a relatively small amount of sulphid sulphur, adsorption was small; consequently, the figures for thiosulphate by the zinc chlorid method are accurate.

R. M. Chapin.—(1) In the estimation of total sulphur I dissolved the sodium peroxid in 50–75 cc. of cold distilled water (best ice-cold) and then pipetted in the sample. I prefer to deliver all samples in this way[2] and a clean pipette should be used each time.

[1] *J. Ind. Eng. Chem.*, 1916, 8: 151, 339.
[2] *Ibid.*, 151.

(2) For thiosulphate sulphur I regard the cadmium chlorid method as treacherous. If carried through cold it seems to give low results, particularly by the referee's modification, while if heat is applied before filtration the results appear erratically high. Zinc chlorid, giving more nearly uniform results under varied manipulation, is more dependable. My modification gives higher results than the referee's method, and since the difference in the titrations varies in proportion to the amount of thiosulphate present, I conclude that adsorption is here a factor to be taken into consideration.

(3) Regarding the so-called "iodin titration methods" originated by Harris, I see no reason to change my previous opinion, namely, that they are to a significant degree unsound and therefore untrustworthy for exact work.

(4) In respect to my own methods, it may be true that their rationale is such as normally to produce slightly high results. But it is certainly true that the gravimetric methods normally yield somewhat low results. I have scrutinized each step of my processes and can find no cause which, given proper execution, will lead to any significant error; consequently, I can only believe that my methods are at least as accurate as the gravimetric methods. The true values very likely lie in between.

D. K. French.—In virtually all cases four independent samples were taken from each solution, made to volume, and the work done upon these different samples. Each figure reported represents the average of five or more determinations made upon the same sample. In other words, on the first sample from Solution 1 the titration was run on two or three 10 cc. portions, one or two 20 cc. portions, possibly a 50 cc. portion, and possibly a 5 cc. portion, the results calculated in all cases and the average reported. When only one or two figures are given, the results on the other samples were so far off and knowledge of the reason why they were so far off was so sufficiently clear that the results were not tabulated. Our laboratory being located in an office building, we are slightly handicapped for want of steam bath conditions, having a very well developed hot plate and sand bath system. This, however, in connection with some of the sulphur figures was not satisfactory, and a certain amount of oxidation took place in the drying. Where any indication of this was noted the results of the determinations were disregarded, as in almost every case they were well off.

Regarding the choice as to methods, the men doing the work are very much in favor of the iodin method, feeling that the results are obtained more rapidly that way.

C. H. Robinson.—Results throughout for sulphid and thiosulphid sulphur by iodin and zinc methods were closely concordant. Cadmium methods invariably gave higher sulphid sulphur and lower thiosulphate sulphur. The iodin methods are more convenient for thiosulphate sulphur, but, if anything, less so for sulphid sulphur. More time is consumed in washing and dissolving sulphur than in washing zinc sulphid. Difficulty was experienced in getting uniform results for calcium oxid by the hydrochloric acid method with Sample 2. The oxidation method gave higher but closely concordant results.

J. J. T. Graham.—Of the methods for thiosulphate sulphur in lime-sulphur, I much prefer the zinc chlorid method, as it has invariably given good results. The cadmium chlorid methods do not give as uniform results in my hands. In the iodin titration method great difficulty was experienced in determining the end point in the monosulphur equivalent titration, as the color of the sodium nitroprussid was discharged very slowly and considerable excess of iodin may be added here. After making a number of preliminary titrations I made the ones reported with extreme care and believe they are as accurate as the method will give. I had no difficulty whatever in determining the end point in the final titration. As the value for thiosulphate sulphur is obtained from the difference between the monosulphur equivalent titration and the total titration, any error in the former will affect the thiosulphate values. In Method

B for thiosulphate sulphur the end points are very easily determined and this method gave results which agreed very closely. Method C for thiosulphate sulphur was very unsatisfactory.

R. N. Miller.—Of the various methods submitted the zinc chlorid method seems to be the least undesirable. In it the chief objections are to be found in the method of making the precipitation, and in handling the filter paper after the precipitation. The manipulation as carried out by Mr. W. J. Morgan of the Insecticide and Fungicide Laboratory of the Bureau of Chemistry, greatly lessens the difficulty. His method is as follows:

Pipette the aliquot into the beaker and add the precipitant without dilution. Move the beaker in a circular movement without slopping on the sides of the beaker. Rinse the sides once and throw immediately on a filter paper. Wash with water. Place the paper opened out on the sides of the beaker in which the precipitation was carried out and rinse the precipitate into the beaker. Add the peroxid, leaving the paper on the sides of the beaker. When the precipitate is all oxidized drop the paper into it and let stand for a little while. Then acidify and filter off the paper and continue as in the method furnished by the referee.

When carried out in this way the filtration is as fast as the cadmium chlorid method. The objection to the cadmium chlorid method that makes it less desirable than the zinc chlorid method is the difficulty experienced in oxidizing the sulphid precipitate. This takes two or three times as much peroxid and considerably longer than the zinc sulphid. Aside from this defect the method seems to be about as good as the zinc chlorid method.

In the iodin titration method the great variation in the results would indicate that even if the method were scientifically correct, it could not be carried out with accuracy except by one skilled in the manipulation of the method.

The end point for the monosulphur equivalent sulphur is not definite without the nitroprussid indicator and the addition of the reagent does not increase the definiteness. If added too soon, the color can be shaken out in 30 seconds. The only way to tell when to add it is to watch the fading of the yellow color, and when the right point is reached there is no further need for an indicator. This point can not be told with definiteness.

O. B. Winter.—Sample 1. This sample exhibited characteristics entirely different from any samples of lime-sulphur solution, either commercial or homemade, that have ever been experienced in the laboratory of the Michigan Agricultural Experiment Station, and some difficulty was found in arriving at the end point for the monosulphur equivalent, especially when using nitroprussid of sodium. The results for thiosulphate by the three methods do not agree satisfactorily. Neither do the results by the iodin or zinc chlorid methods agree so well as they should. This variation in the results is believed to be due to some peculiarity in the sample. Two separate solutions of Sample 1 were prepared, one portion being analyzed immediately and the other 12 hours after preparation. The second solution was kept in a well-stoppered flask and remained perfectly clear until analyzed.

Samples 2 and 3. The results on both samples by all three methods are practically the same, the greatest variation in the averages of all the results being 0.06 per cent. The difference between the maximum and minimum results by the iodin and zinc chlorid methods on these two samples is 0.08 per cent.

Comments: (1) In using sodium nitroprussid as an indicator for the end point in the monosulphur titration by the iodin method, it was found necessary to add the iodin very slowly, drop by drop, stirring vigorously after each addition, as the blue color is discharged very slowly. There seems to be no special advantage in using the nitro-

prussid, for, if one is careful, the end point can be determined very accurately without the indicator.

(2) The results by the cadmium chlorid method were not, generally, so satisfactory as by the two other methods. On Sample 1 the results by this method were higher and on Samples 2 and 3 lower than by the iodin or zinc chlorid method. The differences, however, were not great in either case. No explanation is offered for the high results, but the lower results may possibly be explained by occlusion. The cadmium sulphid precipitate is much more flocculent than the zinc chlorid precipitate. It is suggested that an approximately N/10 solution of cadmium chlorid be used and that the solution be stirred vigorously during the addition of cadmium chlorid.

(3) In point of accuracy there is very little difference between the three methods, a fact that has been well substantiated by previous collaborative work and by a large amount of unpublished work performed in the laboratory of the Michigan Agricultural Experiment Station. The iodin method has many advantages over the others, especially in the time required to complete an analysis, and on this account, without sacrificing accuracy, is preferable.

R. C. Roark.—The use of sodium nitroprussid enables the analyst to get a more accurate and definite end point in the titration for monosulphur equivalent, but 0.1–0.2 cc. of N/20 iodin solution is as close as either the monosulphur equivalent or thiosulphate titration can be made according to the Harris-Averitt method, even with the use of sodium nitroprussid and starch paste to indicate the end points.

I regard the method of determining sulphid sulphur by weighing the sulphur precipitated from solution by iodin as worthless, and if it is oxidized to sulphate and weighed as barium sulphate the method is more tedious and less accurate than the zinc chlorid method[1].

I do not believe that the analysis of a lime-sulphur solution by the zinc chlorid method will consume any more time (exclusive of evaporations, which may be done overnight) than when made according to the iodin titration method. The only determination common to the two methods which can be made in less time by the iodin titration method than by the zinc chlorid is that of thiosulphate sulphur, and this saving of time is offset by the extended period through which the precipitated sulphur in the determination of sulphid sulphur must be allowed to stand before it can be filtered with any approach to accuracy.

The method for total sulphur has been criticized because of unnecessary manipulation. To obtain accurate results it is necessary to remove silica from a solution before determining sulphates. The method recommended by the referee, which is the procedure of Johnston and Adams[2], has been adopted by the association for the determination of large amounts of sulphate in water[3].

In regard to the determination of lime, it is unnecessary to go through the steps for the removal of iron and aluminium, as they are present only in mere traces, if at all, in lime-sulphur solution.

In regard to the cadmium chlorid method, the work this year shows that it possesses some disadvantages and no advantages not possessed by the zinc chlorid method.

In conclusion, I am strongly of the opinion that the zinc chlorid methods, as presented to the association this year, together with certain precautions noted in this report, are the most accurate ones on which any cooperative work has been done, and should be adopted as official by the association.

---

[1] *J. Assoc. Official Agr. Chemists*, 1915, **1**: 76.
[2] *J. Am. Chem. Soc.*, 1911, **33**: 844.
[3] *Assoc. Official Agr. Chemists, Methods*, 1916, 44.

PREPARATION OF AMMONIACAL ZINC CHLORID SOLUTION.

The preparation of ammoniacal zinc chlorid has been studied by many including: Sutton[1], Richardson and Aykroyd[2], McDonnell[3], Blockey and Mehd[4], Proctor[5], McCandlish and Wilson[6], and Bennett[7].

From a consideration of the literature and the reports of collaborators, it is recommended that the method of preparation of the ammoniacal zinc chlorid solution include a statement of the amount of ammonia to be added.

To test the effect of zinc chlorid solutions made up in different ways upon the determinations of sulphid and thiosulphate sulphur, the lime-sulphur solutions sent out for cooperative study were analyzed by the zinc chlorid method, using the following zinc chlorid solutions: (a) A concentrated solution prepared by dissolving 225 grams of zinc chlorid in water, adding 465 cc. of ammonia water (sp. gr. 0.90) and diluting to 1 liter; (b) the solution recommended in this year's instructions, containing 50 grams of zinc chlorid, 50 grams of ammonium chlorid and 120 cc. of ammonia water (sp. gr. 0.90) per liter; and (c) a N/10 solution prepared essentially as directed by Bennett[8], containing 6.8 grams of zinc chlorid, 50 grams of ammonium chlorid and 25 cc. of ammonia water (sp. gr. 0.90) per liter.

Results are as follows:

Comparative results for sulphid and thiosulphate sulphur in A. O. A. C. lime-sulphur samples, using different zinc chlorid solutions.

LIME-SULPHUR	SULPHID SULPHUR			THIOSULPHATE SULPHUR		
	(a)	(b)	(c)	(a)	(b)	(c)
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Solution 1	8.61	8.67	8.82	0.10	0.09	0.10
Solution 2	4.44	4.70	4.61	3.97	4.09	4.14
Solution 3	22.47	22.36	----	0.68	0.68	----

From these results it is seen that the figures obtained with different zinc chlorid solutions do not differ more than duplicate determinations made with the same solution often do.

[1] Sutton. Volumetric Analysis. 10th ed., 1911, 342.
[2] *J. Soc. Chem. Ind.*, 1896, **15**: 171.
[3] U. S. Bur. Chem. Bull. **152**: 70.
[4] *J. Soc. Chem. Ind.*, 1912, **31**: 369; *J. Am. Leather Chem. Assoc.*, 1914, **9**: 176.
[5] Leather Industries Laboratory Book on Analytical and Experimental Methods. 2d ed., 1908, 55.
[6] *J. Am. Leather Chem. Assoc.*, 1913, **8**: 28; 1914, **9**: 203, 205.
[7] *Ibid.*, 1916, **11**: 110, 112.
[8] *Ibid.*, 1916, **11**: 112.

DISCUSSION.

In considering a method for the analysis of a commercial product the first question to consider is—are any substances present that will interfere with the method and vitiate the results? This is particularly important when the material under examination is a solution, as many substances exist in solution that have never been isolated in the pure form.

Hence, in considering different methods for the analysis of lime-sulphur solution it is first necessary to take into account all the different compounds that can exist in such a solution prepared by any of the methods ordinarily employed.

RECENT LITERATURE ON LIME-SULPHUR SOLUTIONS.

For those who may be interested the following references to articles on the composition or analysis of lime-sulphur solutions are given: Averitt[1], Roark[2], Thompson and Whittier[3], Ramsay[4], Auld[5], Van Slyke[6], Tartar[7], Eyre and Salmon[8], Oberfell[9], Len[10], Proctor[11], Chapin[12], Green[13], and Blumenthal and Averitt[14].

AMENDED WORDING OF LIME-SULPHUR METHODS.

The following methods are exactly the same in principle as those previously printed[15]. Certain precautions have been added, however, and the descriptions made fuller, so that it is believed the methods here given will be easier to follow.

LIME-SULPHUR SOLUTIONS.

PREPARATION OF SAMPLE.

Weigh 10 grams of the solution in a weighing pipette, transfer to a 250 cc. graduated flask, and immediately dilute to the mark with recently boiled and cooled water. Mix thoroughly and transfer to a number of small bottles, entirely filling them, and avoiding contact of the solution with air as much as possible. Stopper the bottles, seal with paraffin and preserve in a dark, cool place.

---

[1] *J. Ind. Eng. Chem.*, 1916, **8**: 624; *J. Assoc. Official Agr. Chemists*, 1915, **1**: 74.
[2] *J. Assoc. Official Agr. Chemists*, 1915, **1**: 76.
[3] Del. Agr. Expt. Sta. Bull. **105**: 5, 29.
[4] *J. Agr. Sci.*, 1914, **6**: (II), 194.
[5] *J. Chem. Soc.*, 1915, **107**: 480.
[6] N. Y. Agr. Expt. Sta. Bull. **319**: 394.
[7] Ore. Agr. Expt. Sta. Res. Bull. **3**: 7.
[8] *J. Agr. Sci.*, 1915–16, **7**: (IV), 473.
[9] *J. Am. Leather Chem. Assoc.*, 1915, **10**: 253.
[10] *J. Soc. Dyers Colourists*, 1914, **30**: 277.
[11] Leather Industries Laboratory Book on Analytical and Experimental Methods. 2d ed., 1908, 56.
[12] *J. Ind. Eng. Chem.*, 1916, **8**: 153.
[13] Union of South Africa, Dept. of Agr., 3rd and 4th Reports of the Director of Veterinary Research, Nov. 1915, p. 175.
[14] *J. Am. Chem. Soc.*, 1916, **38**: 1701.
[15] *Assoc. Official Agr. Chemists, Methods*, 1916, 76.

TOTAL SULPHUR.—OFFICIAL.

DETERMINATION.

Dissolve 2 or 3 grams of sodium peroxid in 50 cc. of cold water in a 250 cc. beaker. Transfer a 10 cc. aliquot of the solution prepared for analysis as directed above to this aqueous solution of sodium peroxid, constantly keeping the tip of the pipette just under the surface of the liquid until necessary to raise it for drainage at the end. Use a clean, dry pipette for measuring each portion[1]. Cover the beaker with a watch glass and heat on the steam bath, with occasional stirring, until all the sulphur is oxidized to sulphate, which is indicated by the disappearance of the yellow color. Wash the watch glass and the sides of the beaker, acidify with hydrochloric acid, evaporate to complete dryness, treat with water acidified with hydrochloric acid, boil, and filter to remove silica. Dilute the filtrate to 300 cc., add 50 cc. of concentrated hydrochloric acid[2], heat to boiling, and precipitate with 10% barium chlorid solution slowly and stirring constantly. This should be added at such a rate that about 4 minutes are required in running in the amount necessary (11 cc. for 1 gram of barium sulphate). The rate is best regulated by attaching a suitable capillary tip to the burette containing the barium chlorid solution. Evaporate to dryness on the steam bath, take up with hot water, filter through a quantitative filter paper, wash until free from chlorids, ignite carefully and heat to constant weight over a Bunsen burner. Calculate the sulphur from the weight of barium sulphate, using the factor 0.13734. Sulphur-free reagents, which can easily be procured, should be used for all work.

SULPHID SULPHUR.—OFFICIAL.

REAGENT.

Ammoniacal zinc chlorid solution.—Dissolve 50 grams of pure zinc chlorid in about 500 cc. of water, add 125 cc. of ammonia water (sp. gr. 0.90) and 50 grams of ammonium chlorid and dilute to 1 liter. (See p. 352.)

DETERMINATION.

To 10 or 15 cc. of water in a small beaker add, as directed under total sulphur, a 10 cc. aliquot of the solution prepared for analysis. Calculate the amount of ammoniacal zinc chlorid solution necessary to precipitate all the sulphur in the aliquot, and add a slight excess. Stir thoroughly, then filter, wash the precipitate 3 or 4 times with cold water, and transfer filter paper and precipitate to the beaker in which the precipitation was made. Cover with water, disintegrate with a glass rod and add about 3 grams of sodium peroxid, keeping the beaker well covered with a watch glass. Warm on the steam bath with frequent shaking until all the sulphur is oxidized to sulphate, adding more sodium peroxid if necessary. Make slightly acid with hydrochloric acid, filter to remove shreds of filter paper, wash thoroughly with hot water, and determine the sulphur in the filtrate exactly as under **VII, 69**[3].

THIOSULPHATE SULPHUR.—OFFICIAL.

To 500 cc. of water in a 200 cc. graduated flask, add, as directed under **VII, 69**[3], 50 cc. of the solution prepared for analysis. Add a slight excess of the ammoniacal zinc chlorid solution and dilute to the mark. Shake thoroughly and filter through a dry filter. To 100 cc. of the filtrate add a few drops of methyl orange or methyl red and exactly neutralize with N/10 hydrochloric acid. Titrate the neutral solution with approximately N/20 iodin solution, **VII, 3 (c)**[4], using a few drops of starch solution

[1] *J. Ind. Eng. Chem.*, 1916, **8**: 152.
[2] *J. Am. Chem. Soc.*, 1911, **33**: 844.
[3] *Assoc. Official Agr. Chemists, Methods*, 1916, 76.
[4] *Ibid.*, 63.

as indicator. From the number of cc. of iodin solution used, calculate the thiosulphate sulphur present, using the factor $As_2O_3 \times 1.2959 =$ thiosulphate sulphur (S).

TOTAL LIME.—OFFICIAL.

To 25 cc. of the solution, prepared as directed under **VII, 68**[1], add 10 cc. of concentrated hydrochloric acid, evaporate to dryness on the steam bath, treat with water and a little hydrochloric acid, warm until all the calcium chlorid is dissolved, and filter from sulphur and any silica that may be present. Dilute the filtrate to a bulk of 200–250 cc., heat to boiling, add a few excess cc. of ammonia, and then an excess of a saturated solution of ammonium oxalate. Continue the boiling until the precipitated calcium oxalate assumes a well-defined granular form, allow to stand for an hour, filter, and wash a few times with hot water. Ignite in a platinum crucible over a blast lamp to constant weight, and weigh as the oxid[1].

SUGGESTIONS FOR FUTURE WORK.

(1) The distillation method is not applicable to London purple without previous destruction of the organic matter present, otherwise the distillate is colored purplish or reddish by the dyes that are carried over in the distillation stream. If the organic matter is destroyed by heating with nitric and sulphuric acids it is easier to proceed with the reduction with potassium iodid and sulphuric acid and determine the arsenic[2].

The referee has tried heating London purple with a mixture of zinc oxid and sodium carbonate in a muffle for the destruction of organic matter, and has found this very satisfactory, no arsenic being lost by volatilization. The sample of London purple used in 1910 for the association work was treated in this way and the total arsenic then determined by the official distillation method. The total arsenic found, calculated as As_2O_3, was 38.15 per cent. The total arsenic found by the present official methods[3] was 38.22 per cent, this being the sum of the average As_2O_3 and As_2O_5, calculated as As_2O_3, found by the cooperators in 1910[4].

The mixture of zinc oxid and sodium carbonate, which is prepared by thoroughly mixing 4 parts of zinc oxid with 1 of dry sodium carbonate, was proposed by Ebaugh and Sprague[5] as a fusion mixture for ores containing arsenic. It has been used successfully by Krickhaus[6] and Low[7].

In analyzing a London purple by this method, the sample should be thoroughly mixed with the zinc oxid-sodium carbonate mixture, and then a layer of the latter put on top, the whole being contained in a shallow porcelain crucible. Place the crucible, uncovered, in the electric muffle and heat gradually, finally for about 15 minutes with full

[1] U. S. Geo. Surv. Bull. **422**: 230.
[2] *Assoc. Official Agr. Chemists, Methods*, 1916, 66.
[3] *Ibid.*, **17** and **19**.
[4] U. S. Bur. Chem. Bull. **137**: 39.
[5] *J. Am. Chem. Soc.*, 1907, **29**: 1475.
[6] *Eng. Mining J.*, 1910, **90**: 357.
[7] A. H. Low. Technical Methods of Ore Analysis. 5th ed., 1911, 47.

heat. This treatment will completely burn off all organic matter without driving off any arsenic. The mass will not fuse with this short heating, and, in fact, should not be allowed even to sinter. After all organic matter is destroyed, transfer to a distillation flask and proceed as usual[1].

(2) The referee has tested the method of Gyory[2] for the titration of arsenic trioxid in hydrochloric acid solution with potassium bromate solution and has obtained excellent results. It is believed that this method should be adopted as an optional official method for the titration of arsenic in the distillate after distillation as arsenic trichlorid.

As an example of the results yielded by this method, the referee obtained 38.24 per cent in the 1910 association sample of London purple as against 38.22 per cent by the present official method and 38.15 per cent by the iodimetric titration of the distillate.

This method has been used very successfully by Nissenson and Siedler[3], Rowell[4], and Schmidt[5] for the determination of antimony. Low[6] includes this method in his book.

Jannasch and Seidel[7] used this method for titrating the arsenic in the distillate in the distillation of arsenic as arsenic trichlorid. They found that the titration was independent of the volume and of the degree of acidity between 10 and 40 per cent. The best results were obtained when from 10 to 25 per cent hydrochloric acid (sp. gr. 1.19) was present. Two or three drops of a 0.1 per cent aqueous solution of methyl orange serve as indicator, the end point being shown by a change from pink to colorless.

The advantages of this method over the iodimetric for determining arsenic in a distillate containing arsenic trichlorid are: (1) No neutralization of the distillate is required. This process takes considerable time and consumes large amounts of alkali. Furthermore, we have found in this laboratory samples of sodium hydroxid, purified from alcohol, that contained appreciable amounts of iodin-consuming substances, necessitating the rejection of the alkali for this purpose. (2) The methyl orange solution is stable, whereas starch solution must be freshly prepared to secure good results. (3) The method is cheaper as regards reagents, no alkali or sodium bicarbonate being used, and potassium bromate being cheaper than the equivalent amounts of iodin and potassium iodid used in preparing standard iodin solution.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 63, **4**.
[2] *Z. anal. Chem.*, 1893, **32**: 415.
[3] *Chem. Ztg.*, 1903, **27**: 749.
[4] *J. Soc. Chem. Ind.*, 1906, **25**: 1181.
[5] *Chem. Ztg.*, 1910, **34**: 453.
[6] A. H. Low. Technical Methods of Ore Analysis. 5th ed., 1911, 34.
[7] *J. prakt. Chem.*, 1915, **91**: 133.

Titration of As^{III} in hydrochloric acid solution with potassium permanganate has been tested by Moser and Perjatel[1], who recommend that the titration be made in the cold, drop by drop, in a solution containing only a slight excess of acid. In the hands of the referee this method was found to be too slow, and to yield erratic results due to indefiniteness in the end point, even when manganese sulphate (see Zimmerman-Reinhardt method for iron[2]) was added to the solution.

(3) Some method should be devised for removing the color from arsenic solutions without loss of arsenic, either by adsorption or oxidation of As_2O_3 to As_2O_5. The referee has tested talcum, U. S. P., and animal charcoal, U. S. P., on acid solutions of London purple, but without effect. The following are suggested as worthy of trial: Blood charcoal, fuller's earth, kaolin and kieselguhr. Blood charcoal was tried by Chapin[3], who found that it oxidized arsenites to arsenates. From fuller's earth Lloyd's reagent, or hydrous aluminium silicate, can be prepared, which would probably decolorize a solution very effectively.

RECOMMENDATIONS.

It is recommended—

(1) That the method for the determination of As_2O_3 in lead arsenate as described on p. 332 be adopted as a tentative method.

(2) That the method for the determination of As_2O_5 in lead arsenate as described on pp. 363–4 be adopted as a tentative method. The method as there given is the same as presented on pp. 332–4, except that a preliminary evaporation with hydrochloric acid is called for, this being necessary to destroy nitrates and peroxids which are sometimes found in commercial samples.

(3) That further study be made of methods for the determination of copper, lead and zinc in such preparations as Bordeaux-lead arsenate, Bordeaux-zinc arsenite, etc.

(4) That the so-called zinc chlorid methods for the analysis of lime-sulphur solution be adopted as official, using the amended wording given on pp. 353–5.

(5) That cooperative work be done on the Gyory method for titrating As^{III} in hydrochloric acid solution with a solution of potassium bromate.

(6) That Method I for total arsenic oxid[4] be dropped. (This method is not published in the *Association of Official Agricultural Chemists, Methods*, 1916.)

---

[1] *Monatsh.*, 1912, **33**: 751.
[2] A. H. Low. Technical Methods of Ore Analysis. 5th ed., 1911, 131.
[3] *J. Ind. Eng. Chem.*, 1914, **6**: 1002.
[4] U. S. Bur. Chem. Bull. **107**, rev.: 28.

(7) That the methods for the determination of moisture, free acetic acid and free ammonia proposed in 1910[1] and adopted as official, final action in 1912[2], be dropped. (These methods are not published in the *Association of Official Agricultural Chemists, Methods*, 1916.)

The following recommendation, which was made in 1915, is renewed for final action:

(8) That all other methods for insecticides and fungicides be adopted as tentative and official as given in the *Association of Official Agricultural Chemists, Methods*, 1916, **VII**, 63–77, except as further modified in this report (see lime-sulphur methods, pp. 353–5).

THE OCCURRENCE AND DETERMINATION OF As^{III} AND As^{V} IN THE PRESENCE OF EACH OTHER IN ARSENICAL INSECTICIDES.

By R. C. Roark[3] (Bureau of Chemistry, Washington, D. C.).

It has been customary, except in the case of London purple, to regard the arsenic in arsenical insecticides as existing either as an arsenate or an arsenite, rather than as a mixture of the two. It has been found, however, from the results of many analyses made in the Insecticide and Fungicide Laboratory, that this assumption is not correct. Even in the cases of lead arsenate and zinc arsenite, in which the total arsenic is commonly reported as arsenic oxid, As_2O_5, and arsenious oxid, As_2O_3, respectively, arsenic has been found in both forms of oxidation.

DIRECT DETERMINATION OF As^{III} IN LEAD ARSENATE.

At the 1915 meeting of the association the author presented a method for estimating As_2O_3 in lead arsenate, but the results obtained by the cooperators by this method were low. This method directed that the sample be boiled a few minutes with dilute sulphuric acid (3 to 4 cc. of concentrated acid to 100 cc. of water), and it was thought that the low results were due to lack of sufficient acid or to insufficient boiling.

The effect of concentration of acid is shown in the following table of results on the 1915 association sample of lead arsenate containing lead arsenite:

---

[1] U. S. Bur. Chem. Bull. **137**: 38.
[2] *Ibid.*, **162**: 49.
[3] Present address, General Chemical Co., Baltimore Works, Baltimore, Md.

TABLE 1.

Effect of acid concentration and time of boiling upon the determination of arsenic trioxid in a mixture of arsenate and arsenite of lead.

WEIGHT OF SAMPLE	CONCENTRATED SULPHURIC ACID	WATER	TIME BOILED	ARSENIC TRIOXID FOUND
grams	*cc.*	*cc.*	*minutes*	*per cent*
2.7	5	75	30	5.80
2.7	10	75	30	7.40
2.7	15	75	30	7.75
2.7	15	90	40	7.75
2.7	15	75	40	7.74
2.7	15	60	40	7.70

The amount of As_2O_3 in this sample, as determined by analysis of the ingredients from which it was prepared, is 7.75 per cent.

Additional tests on the time of boiling showed that 30 minutes were sufficient, the time being taken when the solution actually began to boil. As a result of these tests the directions given in the 1915 report on insecticides were changed to the following:

TOTAL ARSENIC TRIOXID IN LEAD ARSENATE.

Weigh an amount of the powdered sample equal to the amount of arsenic trioxid to which 1000 cc. of the iodin solution are equivalent. Transfer to a 200 cc. graduated flask, add 100 cc. of dilute sulphuric acid (water, 85 cc.; concentrated sulphuric acid, 15 cc.), and boil for 30 minutes. Cool, make to volume, shake thoroughly, filter through a dry filter, take 100 cc. of the filtrate, nearly neutralize with a saturated solution of sodium or potassium hydroxid, using phenolphthalein as indicator (if the neutral point is passed make acid with sulphuric acid again), complete the neutralization with sodium bicarbonate, add 4 or 5 grams in excess, and titrate with N/20 iodin solution in the usual way. The number of cc. of iodin solution used in this titration multiplied by 0.2 gives the per cent of arsenic trioxid in the sample.

This method is essentially the same as that used by Haywood and McDonnell[1] in their investigation of lead arsenates found on the market, except that a greater volume of acid is used and the time of boiling is shortened.

The results obtained on 100 commercial lead arsenates by this method are shown in Table 5. Thirty-eight samples contained no arsenic trioxid, twenty-seven had less than 0.10 per cent, fourteen had from 0.10 to 0.19 per cent, six contained from 0.20 to 0.29 per cent, five contained from 0.30 to 0.49 per cent, eight contained from 0.50 to 0.99 per cent, while two contained over 1 per cent.

The ordinary form of lead arsenite is $Pb_3(AsO_3)_2$. Assuming all the As_2O_3 present to be combined in this form, it is seen that a number of

[1] U. S. Bur. Chem. Bull. **131**: 8.

commercial lead arsenates contain appreciable quantities of lead arsenite, for the amount of lead arsenite would be about 4.5 times the arsenic trioxid present.

Of fifty commercial lead arsenates examined, Haywood and McDonnell[1] found only two to contain more than a trace of As_2O_3, and one of these samples was labeled lead arsenite. This sample contained 16.31 per cent of As_2O_5, and 10.01 per cent of As_2O_3; while the other sample contained only 3.91 per cent of As_2O_5, and 40.44 per cent of As_2O_3, all results being calculated on the dry basis. The water-soluble arsenic of both of these samples was high, running 5.56 and 3.28 per cent, respectively, calculated as As_2O_3. This would indicate that all the As_2O_3 in these samples was not present as lead arsenite, but perhaps as sodium or some other soluble arsenite, for the water-soluble arsenic of $Pb_3(AsO_3)_2$ (determined according to the tentative association method for Paris green) is only 0.23 per cent.

Of eleven commercial samples of sodium arsenate examined, Haywood and McDonnell[2] found only traces of As_2O_3 in two or three. This would indicate that As_2O_3 is more likely to be present in a lead arsenate made by some process other than where lead nitrate or acetate is precipitated with sodium arsenate.

This method is not applicable if much nitrate is present, as the nitric acid liberated oxidizes some of the As_2O_3 to As_2O_5, in which form it is not titrated with the iodin solution. To test the action of nitrates, sodium nitrate was added to the 1915 association sample of lead arsenate with lead arsenite in amounts equivalent to 5 and 10 per cent of the whole. Results are as follows:

TABLE 2.

Effect of nitrates upon the determination of arsenic trioxid in a mixture of arsenate and arsenite of lead.

SODIUM NITRATE	CONCENTRATED SULPHURIC ACID	WATER	TIME BOILED	ARSENIC TRIOXID FOUND
per cent	*cc.*	*cc.*	*minutes*	*per cent*
0.00	15	85	30	7.79
				7.73
5.00	15	85	30	7.35
				7.45
10.00	15	85	30	6.71
				6.53

These results show that the method is not applicable in the presence of appreciable quantities of nitrate, but we have found very few com-

[1] U. S. Bur. Chem. Bull. **131**: 9.
[2] *Ibid.*, 16.

mercial lead arsenates to contain more than a trace of nitrate. Haywood and McDonnell[1] found nineteen out of fifty commercial lead arsenates to contain nitrates in small amounts.

DIRECT DETERMINATION OF As^V IN ZINC ARSENITE.

For determining As_2O_5 in zinc arsenites the method presented to the association in 1915 for the determination of As_2O_5 only in lead arsenate was used. As shown later in this paper, this method is not accurate in the presence of nitrates or peroxids, but they are not present in commercial zinc arsenites. Iron salts are always present, but only in traces. The C. M. Smith method, modified[2] was used in determining the arsenic trioxid, and the total arsenic was determined by dissolving the sample in acetic acid, precipitating zinc as the oxalate, and determining arsenic in the filtrate after reduction with potassium iodid and sulphuric acid according to the method of Gooch and Browning[3], except that sodium thiosulphate was used, as suggested by Haywood[4], to discharge the iodin remaining in solution instead of sulphurous acid. This method was presented to the association in 1915, but was recommended to be discarded because antimony is determined by it in addition to arsenic and only the total arsenic was desired. Each of these methods will determine antimony, so that the results are comparable whether or not antimony is present, which we know is the case in certain samples.

TABLE 3.

Results on commercial zinc arsenites (dried samples).

MANUFACTURER	ORIGINAL FORM OF SAMPLE	LABORATORY NUMBER	ARSENIC PENTOXID ONLY	ARSENIC TRIOXID ONLY	TOTAL ARSENIC CALCULATED AS As_2O_3	As_2O_3+ As_2O_5 CALCULATED AS As_2O_3	DIFFERENCE
			per cent	*per cent*	*per cent*	*per cent*	*per cent*
A	Powder	18985	1.75	40.40	41.75	41.91	−0.16
A	Paste	22308	1.16	40.15	41.15	41.15	±0.00
A	Powder	22973	1.29	41.10	42.28	42.21	+0.07
A	Powder	23034	1.63	40.43	41.85	41.83	+0.02
A	Paste	24949	0.32	42.80	43.20	43.08	+0.12
A	Paste	24953	2.05	40.70	42.30	42.46	−0.16
A	Powder	25188	0.72	40.81	41.50	41.43	+0.07
B	Powder	16151	0.90	36.90	37.23	37.67	−0.44
B	Powder	16586	1.31	36.23	37.43	37.36	+0.07
C	Powder	19649	1.98	40.20	41.53	41.90	−0.37

The results are presented in Table 3. It is seen that all commercial zinc arsenites contain some arsenic in the pentavalent form and in rela-

[1] U. S. Bur. Chem. Bull. **131**: 9.
[2] *Assoc. Official Agr. Chemists, Methods*, 1916, 7.
[3] *Am. J. Sci.*, 1890, 3rd ser., **40**: 66.
[4] U. S. Bur. Chem. Bull. **105**: 167.

tively large amounts in some cases. The sum of the separate determinations of As_2O_5 and As_2O_3, calculated to a common basis of As_2O_3, checks the total arsenic, also calculated as As_2O_3 in nearly all the samples.

THIOSULPHATE METHOD FOR THE DETERMINATION OF As^V, AND ITS APPLICABILITY TO COMMERCIAL LEAD ARSENATES.

This method, which is based on the reaction

$$As_2O_5+4HI=As_2O_3+2H_2O+I_2$$

which takes place in acid solution, and the titration of the liberated iodin with standard thiosulphate solution, was first studied by Naylor[1]. He found that the concentration of the hydriodic acid was important, the greatest reduction being effected with solutions containing not less than 20 per cent of hydriodic acid. Phosphates appeared to retard the reduction, and ferric chlorid affected both the hydriodic acid and the thiosulphate solution used in titrating the liberated iodin. Naylor's procedure in quantitative work was as follows:

> An amount of arsenate equivalent to 0.03–0.05 gram of arsenic acid was dissolved in just sufficient water or dilute hydrochloric acid, 5 cc. of 20% hydriodic acid were added, and the iodin titrated with N/10 thiosulphate solution in an atmosphere of carbon dioxid. Fifteen minutes were allowed after decoloration of the solution before taking the final burette reading. The solution of hydriodic acid was prepared by dissolving 34 grains of potassium iodid in 100 cc. of water and adding 25 cc. of hydrochloric acid (sp. gr. 1.16).

As a qualitative test, this method would detect 0.1 mg. of As_2O_5 in the presence of 1 gram of As_2O_3.

Williamson[2] found that the reduction is complete only in strongly acid solution, and that if such a solution be diluted the reverse action takes place to a certain extent. Sulphuric acid could be used instead of hydrochloric. Williamson called attention to the error caused by the presence of nitrates, which is quite large when the sample is heated with potassium iodid and hydrochloric acid, but is not appreciable if the determination is carried through in the cold.

This method has been studied also by the following: Gooch and Morris[3]; Hooper[4]; Krickhaus[5]; Howard[6]; Rupp and Lehmann[7]; Lehmann[8]; Herroun[9]; Weller[10]; Knorre[11]; Yockey[12]; Kolb and Formhals[13].

[1] *Pharm. J. Trans.*, 1879, 3rd ser., **10**: 441.
[2] *J. Soc. Dyers Colourists*, 1896, **12**: 86.
[3] *Z. anorg. Chem.*, 1900, **25**: 227.
[4] *Institution of Mining and Metallurgy Transactions*, 1908, **17**: 331.
[5] *Eng. Mining J.*, 1910, **90**: 357.
[6] *J. Am. Chem. Soc.*, 1908, **30**: 378.
[7] *Apoth. Ztg.*, 1911, **26**: 203.
[8] *Ibid.*, 1912, **27**: 545.
[9] *Chem. News*, 1882, **45**: 101.
[10] *Ann.*, 1882, **213**: 364.
[11] *Z. angew. Chem.*, 1888, 155.
[12] *J. Am. Chem. Soc.*, 1906, **28**: 1435.
[13] *Z. anorg. Chem.*, 1908, **58**: 189.

In order to test the statement of Williamson[1] that nitrates cause only a slight error in this method if the determination be made in the cold, amounts of sodium nitrate equal to 5 and 10 per cent, respectively, of the total sample were added to lead arsenate and the analysis carried through as directed in the 1915 report on insecticides[2]. The same series was also run through after evaporation to complete dryness with hydrochloric acid. Results were as follows:

TABLE 4.

Effect of nitrates upon the determination of pentavalent arsenic by Naylor's method.

SODIUM NITRATE PRESENT	N/20 THIOSULPHATE USED	
	Not evaporated	Evaporated
per cent	*cc.*	*cc.*
0.00	65.30	65.30
	65.30	65.30
5.00	68.60	65.20
	69.00	65.30
10.00	86.20	65.20
	79.40	65.30

This shows that nitrates even at ordinary temperature liberate iodin from potassium iodid in hydrochloric acid solution, but that all nitric acid is expelled by evaporating to dryness on the steam bath with an excess of hydrochloric acid. Evaporation with hydrochloric acid will also decompose lead peroxid which is sometimes present in lead arsenates prepared by roasting lead oxid and arsenic trioxid. Ferric chlorid is not removed by this treatment and will affect the results, but it is never present in more than a trace in commercial lead arsenates.

In Table 5 are shown results on commercial lead arsenates by the thiosulphate method proposed in 1915 and also by the modified method in which the sample is first evaporated with hydrochloric acid.

The directions for the modified method are as follows:

TOTAL ARSENIC PENTOXID.

REAGENTS.

Starch solution.—Prepare as directed under Paris green[3].

Standard iodin solution.—Prepare as directed under Paris green, but calculate in terms of As_2O_5[3].

[1] *J. Soc. Dyers Colourists*, 1906, **12**: 86.
[2] *J. Assoc. Official Agr. Chemists*, 1917, **3**: 157.
[3] *Assoc. Official Agr. Chemists, Methods*, 1916, 63.

STANDARD THIOSULPHATE SOLUTION.

PREPARATION OF SOLUTION.

Prepare an approximately N/20 solution as follows:

Weigh 13 grams of crystallized C. P. sodium thiosulphate, dissolve in water which has been recently boiled and cooled, filter, and make to volume in a 1 liter graduated flask, using water that has been recently boiled and cooled. To standardize this solution, proceed as follows:

(A) Dissolve about 0.7 gram of C. P. dilead arsenate ($PbHAsO_4$) in 50 cc. of concentrated hydrochloric acid in an Erlenmeyer flask. If necessary to effect solution, heat on the steam bath, keeping the flask covered with a watch glass to prevent evaporation of the acid. Cool to 20–25°C., add 10 cc. of potassium iodid solution (20 grams of potassium iodid per 100 cc.) and 50 cc. (or more if necessary to produce a clear solution) of ammonium chlorid solution (25 grams of ammonium chlorid per 100 cc.), and immediately titrate the liberated iodin with the thiosulphate solution, until the solution is colorless, using starch paste as an indicator near the end point. From the weight of lead hydrogen arsenate and the number of cc. of sodium thiosulphate solution used, calculate the value of the latter in terms of As_2O_5. (As_2O_5 in $PbHAsO_4$ = 33.11 per cent.)

(B) Titrate 50 cc. of the standard iodin solution, to which has been added 50 cc. of concentrated hydrochloric acid and 10 cc. of the 20% potassium iodid solution, with the thiosulphate solution, to a colorless solution, using starch paste as an indicator near the end point, and from the ratio of the two solutions, and the value of the iodin solution in terms of As_2O_5 calculate the value of the thiosulphate solution in terms of As_2O_5.

The values obtained by these two methods of standardization should check very closely. The value obtained by procedure (A) is to be preferred. Pure dilead arsenate may be prepared by pouring a solution of lead nitrate into a solution of potassium dihydrogen arsenate (KH_2AsO_4), which should be in excess. The precipitate should be collected by filtration, dissolved in the smallest possible quantity of boiling nitric acid (1 to 4), and this solution then poured into a large quantity of distilled water. The precipitate which results should be collected and dried at 110°C.

DETERMINATION.

Weigh an amount of the powdered sample equal to twice the amount of arsenic pentoxid to which 100 cc. of the thiosulphate solution are equivalent. Transfer to a 400 cc. beaker, add 25–30 cc. of concentrated hydrochloric acid and evaporate to complete dryness on the steam bath. Take up the residue in 50 cc. of concentrated hydrochloric acid, warming to effect solution (beaker must be kept covered to prevent evaporation), and proceed as directed under standardization (A). The number of cc. of thiosulphate solution used in the titration, divided by 2, represents directly the per cent of arsenic pentoxid in the sample.

The great value of this method lies in the saving of time effected by its use. The author has found that a number of determinations may be carried through, from weighing out the samples to entering the results, in an average time of 8 minutes for each determination. This is exclusive of the time necessary to evaporate to dryness with hydrochloric acid, but this evaporation may easily be done overnight, as it does not require any attention on the part of the analyst.

TABLE 5.

Results on commercial lead arsenates (dried samples).

MANUFACTURER	ORIGINAL FORM OF SAMPLE	LABORATORY NUMBER	As_2O_5 ONLY	As_2O_5 ONLY, WITHOUT EVAPORATION	As_2O_5 ONLY, WITH EVAPORATION	DIFFERENCE, COLUMN 5 MINUS COLUMN 6	TOTAL ARSENIC (GOOCH-BROWNING REDUCTION METHOD) CALCULATED AS As_2O_5	SUM OF As_2O_5 PLUS As_2O_5 CALCULATED AS As_2O_5	DIFFERENCE, COLUMN 8 MINUS COLUMN 9
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A	Paste	15952	3.54	----	----	----	----	----	----
B	Paste	23169	1.96	----	----	----	----	----	----
C	Paste	13890	0.00	----	----	----	----	----	----
C	Paste	22799	0.39	----	----	----	----	----	----
C	Paste	22994	0.02	----	----	----	----	----	----
C	Paste	23133	0.02	29.55	28.00	1.55	27.90	28.03	−0.13
C	Paste	23218	0.02	----	----	----	----	----	----
C	Paste	23414	0.16	29.48	27.85	1.63	27.80	28.03	−0.23
C	Powder	8032	0.00	----	----	----	----	----	----
C	Powder	19136	0.20	----	----	----	----	----	----
C	Powder	23132	0.00	----	----	----	----	----	----
C	Powder	23134	0.00	----	----	----	----	----	----
C	Powder	23224	0.37	----	----	----	----	----	----
C	Powder	23608	0.06	----	----	----	----	----	----
C	Paste	20360	0.06	----	----	----	----	----	----
D	Paste	22854	0.00	----	----	----	----	----	----
D	Paste	23239	0.00	----	----	----	----	----	----
D	Paste	23347	0.00	----	----	----	----	----	----
D	Paste	13889	0.00	----	----	----	----	----	----
E	Paste	19231	0.00	29.13	28.28	0.85	28.23	28.28	−0.05
E	Paste	22885	0.18	----	----	----	----	----	----
E	Paste	22886	0.50	----	----	----	----	----	----
E	Paste	22888	0.50	----	----	----	----	----	----
E	Paste	22971	0.61	29.34	28.93	0.41	29.53	29.64	−0.11
E	Paste	23033	0.37	----	----	----	----	----	----
E	Paste	23236	0.07	----	----	----	----	----	----
E	Paste	23346	0.10	30.78	30.03	0.75	30.55	30.15	+0.40
E	Powder	19312	0.00	----	----	----	----	----	----
E	Powder	21079	0.02	32.60	31.25	1.35	31.42	31.28	+0.14
E	Powder	22887	0.00	----	----	----	----	----	----
E	Powder	23032	0.00	----	----	----	----	----	----
E	Powder	23412	0.13	29.98	28.68	1.30	28.95	28.83	+0.12
E	Paste	19264	0.13	28.23	27.88	0.35	27.95	28.03	−0.08
F	Paste	22911	0.12	----	----	----	----	----	----
F	Powder	17726	0.05	----	----	---	----	----	----
F	Powder	17989	0.02	----	----	----	----	----	----
F	Powder	20479	0.00	32.73	32.23	0.50	32.33	32.23	+0.10
F	Powder	22417	0.15	----	----	----	----	----	----
F	Powder	22795	0.17	----	----	----	----	----	----
F	Powder	22910	0.50	----	----	----	----	----	----

TABLE 5.—Continued.

MANUFACTURER	ORIGINAL FORM OF SAMPLE	LABORATORY NUMBER	As_2O_3 ONLY	As_2O_5 ONLY, WITHOUT EVAPORATION	As_2O_5 ONLY, WITH EVAPORATION	DIFFERENCE, COLUMN 5 MINUS COLUMN 6	TOTAL ARSENIC (GOOCH-BROWNING REDUCTION METHOD) CALCULATED AS As_2O_5	SUM OF As_2O_3 PLUS As_2O_5 CALCULATED AS As_2O_5	DIFFERENCE, COLUMN 8 MINUS COLUMN 9
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
F	Powder	23050	0.53	----	----	----	----	----	----
F	Powder	23074	0.23	----	----	----	----	----	----
F	Paste	22870	0.45	----	----	----	----	----	----
G	Paste	23336	0.75	30.45	30.20	0.25	30.78	31.07	−0.29
G	Paste	23401	0.65	28.85	28.55	0.30	28.97	29.30	−0.33
G	Paste	22898	0.15	----	----	----	----	----	----
H	Paste	23129	0.00	----	----	----	----	----	----
H	Paste	23508	0.00	----	----	----	----	----	----
H	Powder	23507	0.00	----	----	----	----	----	----
H	Powder	23540	0.05	----	----	----	----	----	----
I	Paste	22902	0.00	----	----	----	----	----	----
J	Paste	16566	0.51	----	----	----	----	----	----
J	Paste	23068	0.41	----	----	----	----	----	----
J	Paste	23151	0.00	----	----	----	----	----	----
J	Paste	23184	0.15	33.78	33.50	0.28	33.18	33.67	−0.49
J	Paste	23226	0.10	----	----	----	----	----	----
J	Paste	23549	0.08	----	----	----	----	----	----
J	Paste	23653	0.08	----	----	----	----	----	----
J	Powder	22962	0.11	----	----	----	----	----	----
J	Powder	23185	0.02	----	----	----	----	----	----
J	Powder	23225	0.05	----	----	----	----	----	----
J	Powder	23548	0.06	----	----	----	----	----	----
K	Powder	19007	0.09	----	----	----	----	----	----
K	Powder	21985	0.00	----	----	----	----	----	----
K	Powder	22480	0.02	----	----	----	----	----	----
K	Powder	22983	0.00	33.27	32.55	0.72	32.53	32.55	−0.02
K	Powder	23144	0.07	----	----	----	----	----	----
K	Powder	23219	0.00	----	----	----	----	----	----
K	Powder	23327	0.00	----	----	----	----	----	----
K	Powder	23416	0.00	33.23	32.88	0.35	32.80	32.88	−0.08
K	Powder	23544	0.00	----	----	----	----	----	----
L	Powder	23046	0.00	----	----	----	----	----	----
M	Paste	23055	0.00	36.80	30.85	5.95	31.00	30.85	+0.15
N	Paste	22792	0.02	----	----	----	----	----	----
O	Paste	22857	0.00	----	----	----	----	----	----
P	Paste	23349	0.12	----	----	----	----	----	----
P	Paste	23504	0.03	----	----	----	----	----	----
P	Powder	16713	0.00	----	----	----	----	----	----
P	Powder	22989	0.02	----	----	----	----	----	----
Q	Paste	23344	0.00	----	----	----	----	----	----

TABLE 5.—Concluded.

MANUFACTURER	ORIGINAL FORM OF SAMPLE	LABORATORY NUMBER	As_2O_3 ONLY	As_2O_5 ONLY, WITHOUT EVAPORATION	As_2O_5 ONLY, WITH EVAPORATION	DIFFERENCE, COLUMN 5 MINUS COLUMN 6	TOTAL ARSENIC (GOOCH-BROWNING REDUCTION METHOD) CALCULATED AS As_2O_5	SUM OF As_2O_3 PLUS As_2O_5 CALCULATED AS As_2O_5	DIFFERENCE, COLUMN 8 MINUS COLUMN 9
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Q	Powder	23011	0.02	----	----	----	----	----	-----
Q	Powder	23415	0.00	----	----	----	----	----	-----
R	Paste	23183	0.22	32.20	31.70	0.50	32.15	31.96	+0.19
R	Paste	23243	0.27	32.58	32.25	0.33	32.20	32.56	−0.36
R	Paste	23367	0.04	----	----	----	----	----	-----
R	Paste	23408	0.29	----	----	----	----	----	-----
R	Paste	23494	0.27	----	----	----	----	----	-----
S	Powder	17716	0.00	----	----	----	----	----	-----
S	Powder	21165	0.02	33.10	32.15	0.95	31.55	32.17	−0.62
T	Paste	23223	0.00	----	----	----	----	----	-----
T	Paste	23420	0.00	----	----	----	----	----	-----
T	Powder	17730	0.00	30.85	29.83	1.02	30.00	29.83	+0.17
T	Powder	23159	0.00	----	----	----	----	----	-----
U	Paste	11551	0.00	23.55	22.10	1.45	21.83	22.10	−0.27
V	Paste	23157	0.03	----	----	----	----	----	-----
V	Paste	23550	0.05	----	----	----	----	----	-----
V	Paste	23636	0.04	----	----	----	----	----	-----
V	Paste	23657	0.16	----	----	----	----	----	-----
V	Powder	23158	0.00	----	----	----	----	----	-----
W	Paste	23519	0.00	----	----	----	----	----	-----

It is seen that the difference in the amount of As_2O_5 determined without and with evaporation with hydrochloric acid (the modified method) is: minimum, 0.25 per cent; maximum, 5.95 per cent; average, 1.04 per cent, being always higher in the method without evaporation, due to the presence of nitrates or peroxids.

The difference in the total arsenic determined by the modified Gooch-Browning method and the sum of the separate determinations of As_2O_3 and As_2O_5 (the latter being determined by the modified or evaporation method), both being calculated as As_2O_5, is: minimum, 0.02 per cent; maximum, 0.62 per cent; average, 0.21 per cent. In practically all cases where the difference is as much as 0.2 per cent the sum of the two forms of arsenic is greater than the total determined directly. This is due to the presence of ferric salts in the sample, causing high results for As_2O_5. The fact that the average discrepancy is only 0.21 per cent shows that the proposed method for As_2O_5 is sufficiently accurate for use as a tentative method for the rapid examination of commercial samples.

SUMMARY.

(1) A method is proposed for the determination of As_2O_3 in lead arsenate which has been shown to give excellent results on known mixtures of lead arsenate and lead arsenite. Of one hundred commercial lead arsenates tested by this method, representing the product of twenty-three leading manufacturers, thirty-eight contained no As_2O_3; forty-seven contained less than 0.30 per cent of As_2O_3 (approximately 1 per cent of the total arsenic present); while fifteen containedAs_2O_3 in amounts ranging from 0.30 to 3.54 per cent. If all the As_2O_3 is combined as lead arsenite, $Pb_3(AsO_3)_2$, then twenty-one of the samples contain as much as 1 per cent of this compound.

(2) Methods for the determination of arsenic and antimony based on the reaction $As_2O_5+4HI=As_2O_3+2I_2+2H_2O$ in acid solution and titration of the liberated iodin with standard thiosulphate solution have been tested, and a modification is proposed that is directly applicable to commercial lead arsenates with an average error of less than 0.2 per cent of As_2O_5.

(3) Ten commercial zinc arsenites, representing the product of three manufacturers, were tested for As_2O_5, which was found in every case, the amounts ranging from 0.32 to 2.05 per cent. In many cases this As_2O_5 is present as lead arsenate (lead being nearly always present in commercial zinc arsenites), while in some instances it is really Sb_2O_5 that is present although reported as As_2O_5.

REPORT ON WATER.

By W. W. SKINNER (Bureau of Chemistry, Washington, D. C.), *Referee.*

During the current year there was developed and published by Samuel Palkin[1] of the Bureau of Chemistry, a method for the separation and determination of lithium, which appeared to be such a decided improvement over the troublesome and disagreeable Gooch amyl alcohol method, the official method of the association, that the referee decided to confine the cooperative work to a thorough test of the accuracy of the new method for the determination of lithium and to determine the effect of the ether-alcohol separation, if any, upon the accuracy of the method for the determination of potassium and sodium. The method depends upon the use of absolute alcohol and ether for the separation of the lithium chlorid from the mixed chlorids, and Palkin found that by observing certain precautions, the separation was so complete that the use of a factor of correction for the solubility of sodium chlorid and potassium chlorid was entirely obviated. This is a decided improve-

[1] *J. Am. Chem. Soc.*, 1916, **38**: 2326.

ment over the amyl alcohol method, in which a factor must be used, and which is likely to be a cause of controversy, especially when, as is not unusual in the determination of lithium in mineral waters, the lithium found is of the same order of magnitude as the factor of correction.

The method is as follows:

The total alkali chlorids are dissolved in a minimum amount of cold water in a tall 200 cc. beaker. About 1.5 cc. will be more than sufficient for 0.5 gram of the salts. One drop of concentrated hydrochloric acid is added and *gradually* 20 cc. of absolute alcohol, the alcohol being dropped into the center of the beaker (not on the sides) while rotating. The sodium and potassium chlorids should be precipitated in a perfectly uniform granular condition. In a similar manner, while rotating the beaker, 60 cc. of ether (sp. gr. at 25°C., 0.716–0.717) are added and the mixture is allowed to stand about 5 minutes, or until the precipitate is well agglomerated and the supernatant liquid almost clear. The beaker is rotated occasionally.

The mixture is then filtered through a weighed Gooch crucible into an Erlenmeyer flask, using a bell-jar arrangement. The beaker is thoroughly washed with a mixture of 1 part alcohol and 4–5 parts ether. A rubber-tipped rod is necessary for this purpose. The precipitate in the Gooch crucible is also well washed and the crucible set aside. The funnel is well washed to remove any lithium therefrom into the flask containing the filtrate.

The filtrate is evaporated to dryness on the steam bath (using a blast). The residue is taken up with 10 cc. of *absolute alcohol*, warming if necessary, so that practically everything passes into solution. If a slight film remains on the bottom of the flask and sides, it is removed by rubbing with a rubber-tipped glass rod. While rotating the flask, 50 cc. of ether (sp. gr. at 25°C., 0.716–0.717) are added. *One drop* of concentrated hydrochloric acid is added, the flask rotated and allowed to stand for 30 minutes. It is well to rotate the flask at frequent intervals. When the fine precipitate has agglomerated (only a very small amount is usually precipitated), it is filtered through the crucible used in the first precipitation into a tall beaker, a bell-jar arrangement being employed. The residue is washed with ether-alcohol mixture, using the same precautions as outlined in the first precipitation. After drying in an oven, the crucible is gently ignited, cooled and weighed.

The ether-alcohol solution of lithium is evaporated on the steam bath. The residue is taken up in a little water and a slight excess of sulphuric acid added. The solution is then carefully transferred to a weighed porcelain or platinum dish, the solution is evaporated as far as possible on the steam bath, and the residue then gently ignited over a flame. By placing the dish on a triangle over an asbestos gauze and using a low flame, the solution can be evaporated without spattering.

The residue is then carefully ignited over a full flame. When charring has occurred, it is well to repeat the ignition with sulphuric acid.

Calculate to lithium, using the factor 0.12625.

Remove the chlorids of sodium and potassium from the Gooch crucible with 25–50 cc. of hot water, collecting the filtrate in a porcelain dish by means of the bell-jar arrangement. Add sufficient platinic chlorid solution (containing the equivalent of 1 gram of metallic platinum, *i. e.*, 2.1 grams H_2PtCl_6 in every 10 cc.) to convert sodium and potassium to their respective double chlorids and evaporate to dryness. Treat the residue with 80% alcohol, filter, and wash until the excess of platinic chlorid and sodium platinic chlorid has been removed. Dry the filter and precipitate, dissolve the residue in hot water, and transfer to a weighed platinum dish. Evaporate on the steam bath, dry for 30 minutes in the oven at 100°C. and weigh as potassium platinic chlorid;

calculate to potassium chlorid, using the factor 0.30673; and to potassium, using the factor 0.16085.

Find the weight of sodium chlorid by subtracting the weight of potassium chlorid from the total weight of the chlorids obtained above. Calculate to sodium, using the factor 0.39343. Report as milligrams of sodium, milligrams of potassium, and milligrams of lithium per 50 cc. of solution.

Two samples were prepared containing known amounts of lithium, potassium and sodium chlorids. Sample 1 contained 1.3 mg. of lithium per aliquot taken for analysis and was assumed to represent an amount which might be expected in a lightly mineralized sample of water. Sample 2 contained 25.7 mg. of lithium per aliquot taken and was assumed to represent about the maximum amount which might be expected in a sample of water taken for analysis.

The samples were sent out to nine analysts who had asked to participate in the cooperative work. Reports have been received from six.

Cooperative work on water.

ANALYST	MILLIGRAMS IN 50 CC.					
	LITHIUM		POTASSIUM		SODIUM	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
W. D. Richardson, Swift & Company, Chicago, Ill.	1.5	25.8	26.4	32.4	77.8	93.6
	1.8	25.8	26.4	32.3	77.4	93.2
	1.4	25.9	26.5	32.1	76.9	92.8
Samuel Palkin, Bureau of Chemistry, Washington, D. C.	1.6	25.4	26.3	31.5	78.1	94.4
	1.5	25.7	26.4	----	77.9	----
	---	25.7	----	31.8	----	94.0
A. N. Bennett, State Water Survey, Urbana, Ill.	1.5	25.1	26.6	31.9	78.1	94.0
	1.5	25.2	26.6	32.0	78.4	93.8
	1.5	25.3	----	32.0	----	94.0
J. W. Sale, Bureau of Chemistry, Washington, D. C.	1.4	25.7	27.6	33.5	76.5	92.1
	1.4	25.6	27.8	33.4	76.4	93.0
	1.3	25.5	27.6	33.6	----	92.5
R. H. Kellner, Bureau of Chemistry, Washington, D. C.	1.3	25.6	26.7	32.4	77.2	92.5
	1.2	25.5	26.9	32.1	77.2	92.8
	1.3	25.6	26.8	31.9	77.3	92.6
W. F. Baughman, Bureau of Chemistry, Washington, D. C.	1.4	25.5	27.0	31.9	77.3	93.7
	1.3	25.3	26.7	32.1	77.5	93.6
Average	1.4	25.5	26.8	32.3	77.4	93.3
Highest	1.8	25.9	27.8	33.6	78.4	94.4
Lowest	1.2	25.1	26.3	31.5	76.4	92.1
Theory	1.3	25.7	26.2	31.4	77.9	93.4

From the tabulated statement it will be noted that the results for lithium by the Palkin method are all that could be desired, but that the

potassium results are consistently high, the average of the work reported by the six analysts being approximately 2.5 per cent higher than the theoretical amount present. It should be noted further that while the variation in potassium amounted to 2.5 per cent of the theoretical amount present, the actual error in weight amounted to only 0.8 mg., an error which for most analytical purposes may be regarded as negligible. The results for lithium are so entirely satisfactory that the referee feels warranted in recommending the method for adoption by the association as an optional official method.

RECOMMENDATION.

The referee recommends the adoption of the method for the determination of lithium, potassium and sodium (per method in the body of the report) as an official method.

This is the first recommendation of a referee on this method, submitted as provided in By-law No. 6 of the association.

The method has not been published heretofore in the proceedings.

REPORT ON THE LIME REQUIREMENT OF SOILS.

By. F. P. Veitch (Bureau of Chemistry, Washington, D. C.), *Referee.*

It is regretted that only a report of progress can be made at this time. Known samples have been secured from the Rhode Island, Pennsylvania, and Maryland station plats, as well as from other soils the general history of which is known for twenty or more years. Samples have also been obtained upon which other investigators have worked, using other methods for determining lime requirements. Large quantities of some of the samples are on hand, and it is proposed to retain these for testing by the methods which may be developed in the future. The referee will be pleased to supply portions from these samples to those who are developing new methods.

The referee has proposed previously that the reaction to phenolphthalein of distilled water which has been in contact with the soil, with frequent shaking, from 16 to 20 hours, be used as the basis for distinguishing acid and basic soils. This standard is based on his experience and observations that nearly all soils which, under general farming conditions, bore a thick, strong, dark-colored stand of red clover, gave a basic reaction by this procedure. Later experience indicates that if the water has a basic reaction to delicate red litmus paper, it may be considered basic even though it is not basic to phenolphthalein.

Holman[1] observed that when the soil extract obtained with the lime

[1] *Science*, 1916, new ser. 44: 311.

water method is colored with dissolved organic matter, the color produced on adding a phenolphthalein solution to the boiling extract frequently fades out if the boiling is continued, but that the extract is positively basic to red litmus paper.

Several investigators, including the referee, have suggested that the lime water method originally proposed gives high results on soils rich in organic matter. The above mentioned fact is one cause for this. Another is the fact, also observed by Holman, that the calcium carbonate dissolved from the soil by the distilled water in contact with it, frequently does not diffuse into the upper layers of the supernatant liquid even on standing overnight. This is especially true of those soils which are but weakly basic in reaction. These two difficulties are eliminated by the modifications proposed in 1916[1].

During the past year the referee's work has been limited to a further study of the lime water method. A number of indicators have been studied to determine which gives the most marked and definite end point with soil extracts. Among those examined were alizarin, cyanin, rosolic acid, tetrabromphenolsulphonephthalein, dinitrobenzoylene urea, paranitrophenol, phenolsulphonephthalein, and thymolsulphonephthalein.

None of the reagents has proved so satisfactory in the referee's hands as carefully washed red litmus paper, which is more sensitive and more nearly indicates exact neutrality than any of the others and is also much more convenient to use.

The lime water method as now operated by the referee is as follows:

LIME WATER METHOD FOR DETERMINING THE LIME REQUIREMENTS OF SOILS.

APPARATUS AND REAGENTS.

The suitability of the glassware, water, indicators, and filter paper must be definitely determined by careful trial. For this purpose place a filter paper in a well-washed funnel and wash it thoroughly 3–5 times with the distilled water. Run through the paper 100 cc. of the distilled water, receiving it in a well-washed beaker which is to be tested. Add to the filtrate 1 or 2 drops of phenolphthalein solution, a piece of the red litmus paper and boil to a volume of 5 cc. There should be no alkaline reaction. Add 1–2 drops of the standard lime water. The reaction to both the indicators should be alkaline.

DETERMINATION OF SOIL REACTION.

Place 10–12 grams of soil in a 100 cc. non-soluble glass flask, add 80–100 cc. of the tested neutral distilled water, stopper, shake thoroughly, and allow to stand 16–18 hours, shake, filter through a well-washed neutral 12.5 cm. filter (No. 588, C. S. & S. folded filter paper is good), rejecting the first 10 cc. of the filtrate and returning the filtrate until practically clear. Place 50–60 cc. of the filtrate in a clean 100 cc. beaker of non-soluble glass and boil to a volume of about 10 cc. Remove from the gauze, place

[1] *Science*, 1916, new ser. **44**: 311.

the beaker on a piece of white paper and add 2 drops of the phenolphthalein solution and carefully observe the color. If a pink color, no matter how faint, develops, the soil is basic. If a pink color does not develop, add a small piece of delicate red litmus paper and allow to stand for 10 minutes. If the litmus paper turns blue, the soil is basic. If it remains red or reddish purple, the soil is acid.

DETERMINATION OF LIME REQUIREMENT.

To several 11.8–12.0 gram portions of acid soil (as indicated by the concentration of the standard lime water solution which varies from 1.18–1.20 grams of calcium oxid per liter) in 100 cc. flasks of non-soluble glass, add 10–15 cc. of distilled water and different quantities of lime water, arbitrarily selected (according to the nature of the soil) and differing from each other by 5 or 10 cc. Close with clean cork stoppers and allow to stand at room temperature with frequent shaking for 2 hours. Dilute to 75 or 80 cc. with distilled water, and allow to stand with frequent shaking for 2 hours. Filter and test the reaction as described under "Determination of Soil Reaction". If any extract is alkaline to either or both indicators, that portion of soil has been rendered basic by the added lime water. If no portion gives a basic reaction, these preliminary tests must be repeated with larger quantities of lime water. The largest quantity still giving an acid reaction and the smallest quantity giving a basic reaction establish limits within which lies the lime requirement of the soil.

With this information as a guide, take fresh portions of the soil and repeat the tests with quantities of lime water differing from each other by 1 or 2 cc. and lying within the limits established by the previous tests. The smallest amount of lime water which gives the characteristic pink or blue color is taken as the lime requirement of the soil. Each cc. of standard lime water is equivalent to a lime (CaO) requirement of 0.01 per cent or of 100 parts of lime (CaO) per 1,000,000 parts of soil.

This procedure has resulted from the trial on numerous samples of several modifications, including treating the soil with the lime water at 60°C. for 2 hours, diluting and allowing to stand from 14 to 16 hours, moistening basic soils with distilled water only, and drying on the steam bath; heating for 2 hours at 60°C., diluting and allowing to stand from 14 to 16 hours.

These procedures all gave higher results on soils rich in organic matter. Some basic soils even appeared to be acid and to have a marked lime requirement. Clays and loams containing no organic matter gave closely agreeing results by all procedures when the final time of standing in contact with distilled water was the same in all cases. It must be remembered, however, that the longer the soil stands in contact with distilled water the lower its apparent lime requirement.

Many soils which are basic to the procedure above described for determining the reaction of soils are decidedly acid and have a high lime requirement when tested by the hydrogen electrode procedure suggested by Sharp and Hoagland[1], or by the freezing point procedure proposed by Bouyoucos[2].

It is desired to point out that this method does not indicate the quan-

[1] *J. Agr. Research*, 1916, **7**: 123.
[2] Mich. Agr. Expt. Sta. Tech. Bull. **27**.

tity of lime necessary to maintain the basic reaction of a soil throughout a growing season or under field or cropping conditions. No method for determining lime requirement can do this.

The method is designed to determine the lime requirement of the sample at the time it is examined. Assuming that the sample is representative, the additional quantity of lime which will be required to maintain a basic reaction in any soil under any given conditions of texture, crop, organic matter, moisture, bacterial activity, etc., can only be estimated. It can not be definitely or even approximately determined.

L. P. Howard (Agricultural Experiment Station, Kingston, R. I.), submitted a paper on "The Relation of the Lime Requirements of Soils to Their Retention of Ammonia"[1] [2].

DRUG SECTION.

No report on medicinal plants and drugs was made by the referee.

REPORT ON SYNTHETIC PRODUCTS.

By W. O. EMERY (Bureau of Chemistry, Washington, D. C.),
Associate Referee.

An adapted method for estimating hexamethylenetetramin in pharmaceutical practice, namely, tablets, was sent to the collaborators.

The method, as developed on numerous controls, took the following form:

REAGENTS.

A. *Modified Nessler's reagent.*—(a) Solution of 10 grams of mercuric chlorid, 30 grams of potassium iodid and 5 grams of acacia in 200 cc. of water, filtered through a pledget of cotton; and (b), solution of 15 grams of sodium hydroxid in 100 cc. of water.

B. *N/10 iodin solution.*

C. *N/20 thiosulphate solution.*

PRELIMINARY TREATMENT.

Ascertain the weight of 20 or more tablets (Sample 19), triturate in a mortar to a fine powder and keep in a small capsule tightly closed with a cork or glass stopper. Weigh out 0.5 gram (1 gram in the case of Sample 20, which consists of about equal parts of hexamethylenetetramin and talc) of the powdered product on a metal scoop or watch glass, transfer with sufficient water to a round-bottomed flask, add additional water to a total volume of 100 cc. and finally 25 cc. of 10% hydrochloric acid. Connect with a reflux condenser (preferably of the worm type) and boil gently for 15 minutes.

Cool, wash out the condenser tube with a little water and transfer the contents of the flask quantitatively to a graduated 250 cc. flask, finally diluting to the mark with water.

---

[1] *Soil Science*, 1918, 6: 405.
[2] Presented by B. L. Hartwell.

METHOD.

With a pipette withdraw 10 cc. (containing, in the case of a pure product, the elements of 0.02 gram of hexamethylenetetramin) of the solution so prepared to a 200 cc. Erlenmeyer flask containing a mixture (chilled in ice-water if available) of 20 cc. of reagent A (a), and 10 cc. of A (b), wash down the neck of the container with a jet of water from the wash bottle and allow to stand for *at least 1 minute.* Add 10 cc. of 40% acetic acid in such a manner that the inside of the neck is completely washed by the reagent, mix quickly and thoroughly by rotating and tilting the flask, and immediately run in from a burette 20 cc. of solution B, then titrate with C, adding 5–10 drops of starch solution toward the end of the operation, to the disappearance of the blue coloration. The final color of the solution is a pale straw-green. If preferred, the end point may be determined by the reappearance of a faint blue coloration, induced by the addition of a drop of iodin.

COMMENTS AND SUGGESTIONS.

The foregoing is essentially a reversal of the procedure first employed by Rupp[1] in the evaluation of mercuric chlorid tablets with formaldehyde and subsequently made use of by Stüwe[2] in the estimation of formaldehyde, formalin and hexamethylenetetramin.

Unfortunately, none of the earlier operators apparently felt the necessity of describing in detail the several steps followed by them, hence the writer was compelled to determine for himself the salient factors bearing particularly on the quantitative side. Briefly, the method involves four principal operations, namely:

(1) Hydrolysis of the hexamethylenetetramin to formaldehyde and ammonia; (2) interaction of formaldehyde with potassium mercuric iodid of reagent A (a) (1); (3) solution of the mercury resulting therefrom; and, (4) titration of the unexpended iodin. From the data thus gained, the quantity of hexamethylenetetramin is readily calculated. The reaction taking place between formaldehyde and potassium mercuric iodid in the presence of caustic alkali is given in the equation:

$$CH_2O+K_2HgI_4+3KOH=Hg+HCO_2K+4KI+2H_2O.$$

In conducting the method proper, unusual care is necessary in adding and mixing the several reagents with the preceding menstruum so that a uniform solution will result. This is effected by judicious rotation and tilting of the flask, and at certain points also by washing down the neck of the container with a fine jet of water. The addition of iodin should follow acidification with the greatest possible dispatch, because long standing of the mixture in the presence of free acetic acid invariably leads to low values for hexamethylenetetramin, due apparently to partial resolution of the colloidal mercury first precipitated. The primary chilling of Nessler's reagent is advocated in order to minimize to the utmost any tendency toward secondary reactions, and also to avoid the

[1] *Arch. Pharm.*, 1906, **244**: 540; 1914, **252**: 430.
[2] *Ibid.*, 1905, **243**: 300; *Pharm. Ztg.*, 1914, **59**: 215.

possible loss of iodin through undue increase in temperature on the addition of acetic acid.

Since the standard iodin (reagent B) has twice the strength of the thiosulphate (reagent C), and 1 cc. of N/10 iodin is equivalent to 0.001167 gram of hexamethylenetetramin (O = 16), the quantity of this product in the aliquot under examination may be readily calculated from the expression:

$$\frac{H - I}{2} \text{ N } 0.001167$$

in which H = number of cubic centimeters of reagent C, equivalent to 20 cc. of reagent B; I = number of cubic centimeters of reagent C required to offset the unexpended iodin; and N = the normality of reagent B.

Before formulation and submission of the foregoing method for collaborative purposes, many experiments were made to the end that any factors, such as the influence of time, temperature, concentration, vehicles and diluents employed in the manufacture of tablets, calculated to affect unfavorably the quantitative results, might be determined and subsequently eliminated, or, as far as possible, counteracted.

Thus, it was found that precipitation of colloidal mercury is practically instantaneous and hence complete after the lapse of one minute from the time the mixture has attained homogeneity. However, since secondary reactions at this point are not to be feared, there can be no objection to allowing the mixture to stand for a longer period, if desired, before the addition of acetic acid.

In order to ascertain to what extent, if any, the final result might be affected by varying the time during which the precipitated mercury is subjected to the solvent action of acetic acid, a series of controls was carried out involving 15 seconds, 1, 2, 3, 4, 5, 10, 20 and 30 minute intervals, on the lapse of which the mixtures were treated immediately with iodin and then titrated as prescribed in the method. The recoveries of hexamethylenetetramin in these tests were 100.1, 99.5, 98.9, 98.5, 97.9, 97.7, 97.3, 96.7 and 96.3 per cent, respectively, thereby showing that protracted contact of the colloidal metal with the acid invariably leads to low values.

That the presence of vehicles or diluents like starch, lactose and acacia has no appreciable effect on the final outcome is clearly shown in recoveries of 99.8, 99.9 and 100.2 per cent of hexamethylenetetramin, respectively, obtained with controls involving the substances in question; hence their elimination from tablets prior to analysis is entirely unnecessary.

Of the dozen or more chemists who indicated a willingness to collaborate, eleven submitted their findings in time for incorporation in

the present report. The data so presented have been arranged in the following tabulated form:

Cooperative results on synthetic products.

ANALYST	CONTROL HEXA-METHYLENE-TETRAMIN	TABLETS NO. 19	MIXTURE NO. 20
	per cent	*per cent*	*per cent*
A. R. Albright, Bureau of Chemistry, Washington, D. C.	99.8	92.8	50.2
V. B. Bonney, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, San Francisco, Cal.	----	90.5	50.0
L. A. Brown, Agricultural Experiment Station, Lexngton, Ky.	99.9	91.6	49.3
J. F. Darling, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	----	88.4	50.0
W. O. Emery, Bureau of Chemistry, Washington, D. C.	99.8	90.7	50.8
C. K. Glycart, U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.	----	90.4	50.5
W. S. Hubbard, Bureau of Chemistry, Washington, D. C.	----	90.6	49.9
H. B. Mead, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, Philadelphia, Pa.	98.3	90.7	51.7
C. B. Morison, Agricultural Experiment Station, New Haven, Conn.	----	90.6	50.1
C. E. Parker, U. S. Food and Drug Inspection Station, Tabor Opera House Building, Denver, Colo.	99.6	91.9	50.6
W. R. Rich, Agricultural Experiment Station, Orono, Me.	----	93.3	50.4
C. D. Wright, Bureau of Chemistry, Washington, D. C.	99.9	91.9	50.6

As above indicated, controls were carried out by some of the workers on various standard brands of the pure product. Number 19 consisted of a certain brand of commercial tablets containing 10 per cent more or less of a vehicle or diluent. Number 20, on the other hand, was a laboratory product obtained by triturating talc and hexamethylenetetramin in a mortar in about equal parts, and presumably, therefore, a more uniform preparation than Number 19. The foregoing percentages are for the most part averages drawn from two or more determinations carried out, if not strictly, in general accordance with the method. Some of the collaborators, however, found time to make additional tests

with a view to betterment in detail, or to ascertain to what extent, if any, changes in the matter of time, temperature, size of aliquot, etc., might affect the final outcome.

As the result of a very interesting series of experiments involving modifications in time and temperature, Mr. Brown concludes that the reaction is not complete under 4 minutes, and that a temperature below 20°C. has a tendency to give low results even when the time is extended to 4 minutes. Accordingly, he believes that the method should read: "Allow the reaction to proceed for at least 4 minutes at a temperature of 20–25°C."

As a matter of curiosity, Mr. Darling fumed a portion of each sample with sulphuric acid, later estimating the ammonia resulting therefrom. The values obtained for hexamethylenetetramin agreed quite well with those reported above.

On account of the relatively small amount of substance represented in the aliquot used, Mr. Mead tried tripling the quantity of hydrolyzed product. Practically the same recoveries were obtained as in the regular way, thus apparently indicating that no greater accuracy is secured by increasing the amount of substance prescribed in the method.

In connection with Mr. Morison's report, the following note was added:

Five-tenths gram of the pure salt was hydrolyzed by boiling with dilute acid under a reflux condenser, essentially as proposed in the cooperative method. The acid solution was then cooled and brought to a volume of 250 cc. An aliquot was transferred to an Erlenmeyer flask and mixed with 25 cc. of approximately normal sodium hydroxid solution, followed by the addition of 25 cc. of N/10 iodin. The resulting mixture was allowed to stand for about 10 minutes to insure completion of the reaction, and then acidified with 30 cc. of approximately normal sulphuric acid. The liberated iodin was thereupon titrated with N/20 thiosulphate.

1 cc. of N/10 iodin = 0.001167 gram of hexamethylenetetramin.

This is an application of the G. Romijn method for formaldehyde. Recoveries by this method were as follows: 20 mg. taken; recovered in four determinations, 20.1, 20.5, 20.2 and 20.3 mg. In a single determination on No. 20, 49.8 per cent recovery was effected.

It is believed that further study should be made of the method as well as of the procedure outlined by Mr. Morison.

No report on medicated soft drinks was presented by the associate referee.

No report on balsams and gum resins was presented by the associate referee.

REPORT ON ALKALOIDS.

By H. C. Fuller (Institute of Industrial Research, Washington, D. C.), *Associate Referee.*

The work included the study of methods for determining atropin in tablets and strychnin in elixirs. The method used for strychnin last year was further studied and a recommendation for its provisional adoption is included in this report.

ATROPIN.

DETERMINATION OF ATROPIN IN TABLETS.

Weigh 25 tablets and introduce directly into a small separator. Moisten with 5 cc. of water. Add 1 cc. of stronger ammonia water. Agitate with 25 cc. of chloroform and allow to stand until separation is complete. Draw off the chloroform into a second separator and repeat the agitation twice more with 25 cc. portions of the solvent. After combining all of the fractions, wash the combined chloroform solutions by agitation with 10 cc. of water and allow to stand 15 minutes. Introduce a pledget of absorbent cotton into the stem of the separator and run off the chloroform into the tared dish, but do not allow the wash water to enter the orifice of the stop-cock. Add 10 cc. of chloroform, and when the water has entirely risen to the surface run off the chloroform into the tared beaker. Wash off the outer surface of the stem of the separator with a little chloroform and then evaporate over a water bath, using a fan or blower and removing from the bath as the last portions evaporate to avoid decrepitation. Check the weight of the atropin by dissolving the residue in neutral alcohol, adding an excess of N/10 sulphuric acid and titrating back with N/50 potassium hydroxid.

Calculate to atropin sulphate (1 cc. of N/50 H_2SO_4 = 0.005741 gram of atropin).

Factor for atropin to atropin sulphate, 1.1695.

Cooperative results on atropin sulphate.

ANALYST	ATROPIN SULPHATE	
	Per cent	Grain per tablet
J. R. Eoff, Bureau of Internal Revenue, Washington, D. C.	2.29	0.01 0.0095[a]
A. W. Hanson, U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.	2.00 1.23	0.0087 0.0053[a]
H. C. Fuller, Institute of Industrial Research, Washington, D. C.	1.99	0.008

[a] By titration.

STRYCHNIN.

DETERMINATION OF STRYCHNIN IN ELIXIR OF IRON AND STRYCHNIN.

Tare a 50 cc. volumetric flask, fill to mark with sample and weigh. Pour into an evaporating dish, wash the flask with water and evaporate the alcohol. Transfer to an 8-ounce Squibb separator. Add an excess of ammonia. Agitate with 25 cc. of chloroform and allow to stand until separation is complete. Draw off the chloroform

into a second separator and repeat the agitation twice more with 25 cc. portions of the solvent. After combining all of the fractions, agitate with 3 portions of 10 cc. each of N/1 sulphuric acid, collecting the acid solutions together in a fresh separator. Discard the chloroform. Treat the acid solution with an excess of ammonia, agitate with 15 cc. of chloroform and allow to stand until separation is complete. Draw off the chloroform into a second separator and repeat the agitation twice more with 15 cc. portions of chloroform. After combining all of the chloroform fractions, wash by agitation with 10 cc. of water and allow to stand 15 minutes. Introduce a pledget of absorbent cotton into the stem of the separator and run off the chloroform into a tared dish, but do not allow the wash water to enter the orifice of the stop-cock. Add 10 cc. of chloroform, and when the water has entirely risen to the surface, run off the chloroform into the tared beaker. Wash off the outer surface of the stem of the separator with a little chloroform and then evaporate over a steam water bath, using a fan or blower and removing from the bath as the last portions evaporate to avoid decrepitation. Dry at 100°C. to a constant weight and weigh as strychnin.

Strychnin to strychnin sulphate, 1.2814, according to U. S. P.

Cooperative results on elixir of iron and strychnin.

ANALYST	STRYCHNIN SULPHATE	
	Per cent	Grain per fluid ounce
Parke, Davis & Co., Detroit, Mich.	0.037 0.035[a]	0.187 0.179[a]
E. K. Nelson, Bureau of Chemistry, Washington, D. C.	0.033 0.034	0.166 0.17
J. B. Luther, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	0.0342 0.0333 0.0318[a] 0.031	0.17 0.166 0.156[a] ----
W. R. Rippetoe, Schieffelin & Co., New York, N. Y.	0.039	0.22
J. P. Street, Agricultural Experiment Station, New Haven, Conn.	0.0375 0.038[a]	0.19 0.194
H. C. Fuller	0.040 0.036	0.20 0.18

[a] By titration.

RECOMMENDATIONS.

It is recommended—

(1) That the methods for the determination of strychnin in tablet triturates be made provisional.

(2) That the method for the determination of strychnin in liquids where it occurs as the only alkaloid be made provisional.

(3) That a further study be made of the method for determining atropin in tablets.

(4) That the work on alkaloids be extended to a study of methods of determination of strychnin and quinin in admixture.

REPORT ON MEDICINAL PLANTS.

By Arno Viehoever (Bureau of Chemistry, Washington, D. C.),
Associate Referee.

The report is divided into three parts:

I. A consideration of a method for the determination of volatile mustard oil found in true mustard and in mustard substitutes.

II. A brief discussion of the determination of ethereal oil in drugs and spices.

III. The adulteration of crude drugs and spices.

PART I.

While the new Pharmacopœia gives a method for the determination of allylisothiocyanate in volatile mustard oil, no method has been given for the liberation of the oil from the mustard seed. The method adopted by the Pharmacopœia for the determination of allylisothiocyanate content is essentially that of the German, Swedish, French, and Japanese Pharmacopœias. It is in principle the method of E. Dietrich[1], as modified by Gadamer[2].

Comparative investigations on the different methods undertaken by different workers[3] showed the advantage and disadvantage of one or the other methods sufficiently, so that no repetition of that work appeared to be warranted. In view, however, of the existing uncertainty as to certain factors which might influence the result, especially conditions of maceration, the following experiments were undertaken with Chinese colza (*Brassica campestris chinoleifera* Viehoever):

(1) Maceration at different temperatures.

(2) Maceration at different intervals, for different periods.

(3) Maceration with and without shaking the maceration mixture.

(4) Maceration with and without addition of alcohol to the maceration liquid before the maceration.

(5) Maceration with *Sinapis alba* (white mustard).

All data indicate that lower results are obtained with prolonged maceration, and the results furthermore indicate that temperature higher than room temperature tends to hasten the liberation of mustard oil. Shaking during the maceration apparently has no decided influence on the result. The addition of alcohol to the maceration liquid before

---

[1] *Helfenberger Annalen*, 1886, **1**: 59.
[2] *Arch. Pharm.*, 1899, **237**: 110.
[3] Wehrmann, Wegener, Braunwarth and Meyer. *Arch. Pharm.*, 1915, **253**: 308.

maceration has given higher results. The question as to whether or not this higher result is due to secondary reaction, possibly the development of allylthiourethan, is under investigation.

The following table gives the results of the collaborators:

Influence of time and temperature of maceration upon yield of volatile mustard oil.

ANALYST	TEMPERATURE (ROOM) 22–27°C.			TEMPERATURE 37°C.				TEMPERATURE 50°C.		
	TIME			TIME				TIME		
	2 HOURS	4 HOURS	6 HOURS	1 HOUR	2 HOURS	4 HOURS	6 HOURS	2 HOURS	4 HOURS	6 HOURS
V. K. Chesnut, Bureau of Chemistry, Washington, D. C.	0.51	0.42	----	0.47	0.45	0.48	----	0.50	0.41	----
	0.53	0.42	----	----	----	0.48	----	0.48	0.41	----
J. F. Darling, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	0.45	0.42	0.38	----	0.44	0.41	0.33	0.48	0.40	0.33
	----	----	----	0.54[a]	0.62[a]	----	----	----	----	----
	----	----	----	0.56[a]	----	----	----	----	----	----
P. L. Gowen, Bureau of Chemistry, Washington, D. C.	0.46	0.37	0.28	----	0.45	0.32	0.29	0.46	0.37	0.28
	0.46	0.37	0.26	----	0.45	0.32	0.27	0.44	0.34	0.24
E. H. Grant, Bureau of Chemistry, Washington, D. C.	0.43	0.63	0.49	----	0.47	0.61	0.67	----	----	----
	0.48	0.55	0.63	----	0.47	0.61	0.67	----	----	----
	----	0.58	----	----	----	0.53	----	----	----	----
E. K. Nelson, Bureau of Chemistry, Washington, D. C.	0.31	0.21	----	----	0.38	0.22	----	----	----	----
	0.30	0.22	----	----	0.37	0.22	----	----	----	----
	----	0.18	----	----	----	----	----	----	----	----
J. R. Rippetoe, and N. Smith, Schieffelin & Co., New York, N. Y.	0.40	0.33	0.25	----	0.41	0.25	0.36	0.58	0.57	0.56
	0.41	0.32	0.23	----	0.40	0.29	0.21	0.57	0.53	0.53

[a] Twenty cc. of alcohol were added before maceration.

The addition of *Sinapis alba* has been tried out, but had no effect on the result.

The following table shows the effect of maceration for various periods of time with and without white mustard:

Effect of white mustard, added to maceration mixture, upon yield of volatile oil.
(Analysts, A. Viehoever and C. O. Ewing.)

MATERIAL	AMOUNT	PERIOD OF MACERATION[a]			
		1 HOUR	2 HOURS	3 HOURS	4 HOURS
	grams	*per cent*	*per cent*	*per cent*	*per cent*
White mustard alone	10	----	0.06	0.06	0.06
Chinese colza alone	10	0.45	0.42	0.40	----
White mustard and Chinese colza	5 of each	----	0.51	0.51	0.51

[a] Temperature of maceration, 37°C.

The addition of tartaric acid had no effect, which is confirmed in the work mentioned in the above article concerning comparative studies.

The powdered seed was usually put through a 1 mm. sieve and then no olive oil was necessary to prevent frothing. Finer ground flour, however, tended to froth.

The best conditions for maceration appeared to be 2 hours at 37°C. Whether or not alcohol should be added to the maceration mixture before maceration has not been definitely decided.

Other modifications are under consideration, *e. g.*, the best conditions to receive the volatile oil, whether ammonia alone or mixed with alcohol or silver nitrate solution; furthermore, whether or not the distillation mixture after addition of silver nitrate solution should best be heated directly for 1 hour on the steam bath, or after standing 12 to 24 hours.

Of special interest is the fact that Leach, in his book on Food Analysis, gives a factor which is about three or four times too high. The original article of Roeser has undoubtedly been misinterpreted. This method gives, as recent investigators have shown, results which agree very well with those obtained with the Dietrich-Gadamer method. High results obtained with the Roeser method may thus often be explained, and it is suggested that statements as to abnormally high amounts found in mustards and mustard substitutes be regarded with suspicion, especially if the Roeser method has been used or if the method used has not been stated.

PART II.

A general method for the determination of volatile oil is very much needed. No standard has yet been adopted as to the amount of volatile oil in drugs and spices, and this naturally would be most desirable in the proper judgment of the strength and quality of such goods. A consideration of the method described in Bureau of Chemistry, Bulletin 107 (Revised), page 163, is of interest. While the results obtained with the method may be correct so far as the non-volatile ether extract is concerned, it is feared that during the evaporation of the ether, and

later on, especially during the drying for 18 hours in the desiccator, appreciable amounts of volatile oil are lost. Although the present method of procedure might give an arbitrary result, knowing the main source of error, it is believed that the method is not altogether satisfactory.

The associate referee has tried by steam distillation to determine the amount of volatile oil in anise and caraway, and drugs of similar nature. The steam is passed through a certain amount of the crushed material and carries with it the ethereal oil, which is collected, salted out, and extracted from solution by means of an organic solvent such as ether, petroleum ether, or carbon tetrachlorid. It may be mentioned here that in some instances the addition of carbon tetrachlorid to the mixture before distillation proved to be successful in speeding the removal of the ethereal oil from the material. The solution of the volatile oil is concentrated on a steam bath to a small quantity, usually to not less than

Determination of volatile oils by spontaneous evaporation of the ethereal

NUMBER	SUBSTANCE	AMOUNT OF SUBSTANCE TAKEN	I	
			WEIGHT IMMEDIATELY AFTER EVAPORATION OF ETHER	
		gram	*gram*	*per cent*
1	Eugenol	0.1676	0.1824	108.8
2	Oil of clove	0.1492	0.1556	104.3
3	Oil of pimenta	0.1394	0.1434	102.9
4	Oil of bay	0.1456	0.1370	94.1
5	Cinnamic aldehyde	0.1585	0.1585	100.0
6	Oil of cassia	0.1908	0.2040	106.9
7	Oil of Ceylon cinnamon	0.1700	0.1636	96.2
8	Oil of anise	0.1574	0.1622	103.1
9	Oil of caraway	0.6262	0.5242	83.7
10	Carvon	0.1628	0.1648	101.2
11	Oil of ginger	0.1784	0.1664	93.3
12	Oil of peppermint	0.1440	0.1274	88.5
13	Menthol	0.1400	0.1330	95.0
14	Camphor	0.3912	0.3836	98.0
15	Thymol	0.1148	0.1224	106.6
16	Oil of eucalyptus	0.1346	0.1216	90.3
17	Oil of turpentine	0.2254	0.1689	74.9
18	Oil of lemon	0.1540	0.1278	83.0
19	Benzaldehyde	0.2158	0.2003	92.8

10 cc. If evaporated down further, one can detect by the odor, or by a rise in the boiling point, that some volatile oil escapes with the organic solvent. The associate referee has tried to decrease the escape of volatile oil by blowing the solvent away with a gentle blast and drying the remaining ethereal oil completely for a few hours in a vacuum desiccator. The product thus obtained is undoubtedly the volatile oil without the

addition of fatty, waxy, or coloring matter, which is obtained in the indirect ether extract method.

Thus far the associate referee has not obtained concordant results between the volatile ether extract and the oil obtained by distillation. Usually the amount of oil found by direct distillation was smaller than by the indirect method.

This observation is confirmed by Hortvet[1], who obtained the amount of volatile oil in cloves by direct distillation with steam and indirectly as volatile ether extract. To show the loss of volatile oil through spontaneous vaporization of the ether and the drying of the ether extract in vacuum for an extended time, the following table is included. It is taken from Reich's work[2], and shows convincingly that the loss of volatile oil always occurs, and that the amount lost depends on the nature of the volatile oil.

solution and subsequent drying of the residue in vacuum.

II		III		IV		V	
WEIGHT AFTER STANDING 30 MINUTES IN DESICCATOR		WEIGHT AFTER STANDING 2 HOURS IN DESICCATOR		WEIGHT AFTER STANDING 24 HOURS IN DESICCATOR		WEIGHT AFTER STANDING 48 HOURS IN DESICCATOR	
gram	*per cent*	*gram*	*per cent*	*gram*	*per cent*	*gram*	*per cent*
0.1746	104.2	0.1721	102.7	0.1661	99.1	0.1610	96.6
0.1486	99.6	0.1450	97.2	0.1420	95.2	0.1386	92.8
0.1394	100.0	0.1356	97.3	0.1314	94.3	0.1282	91.9
0.1290	88.6	0.1240	85.2	0.1034	71.0	0.0944	64.9
0.1585	100.0	0.1577	99.5	0.1481	93.4	0.1451	91.6
0.1940	101.7	0.1908	100.0	0.1840	96.4	0.1810	94.8
0.1600	94.1	0.1564	92.0	0.1456	85.7	0.1420	83.5
0.1554	98.7	0.1549	98.4	0.1524	96.8	0.1458	92.6
0.5197	83.0	0.5162	82.4	0.4874	77.8	0.4266	68.1
0.1568	96.3	0.1548	95.1	0.1478	90.8	0.1348	82.9
0.1649	92.4	0.1622	90.9	0.1498	83.9	0.1460	81.8
0.1208	83.8	0.1194	82.9	0.0964	66.9	0.0844	58.6
0.1264	90.3	0.1244	88.9	0.1184	84.6	0.1084	77.4
0.3630	92.8	0.3472	88.8	0.2832	72.4	0.2316	59.2
0.1100	95.8	0.1070	93.2	0.1050	91.4	0.1060	92.3
0.1060	78.8	0.0988	73.4	0.0478	35.5	0.0298	22.1
0.1558	69.1	0.1474	65.4	0.0734	32.5	0.0640	28.3
0.1230	79.9	0.1196	77.7	0.0716	46.5	0.0434	28.2
0.1758	81.2	0.1638	75.9	0.1158	53.7	0.0958	44.4

To overcome the obvious errors through evaporation, the oil may be distilled directly and then separated mechanically and the volume determined. From this, together with the specific gravity, the actual

[1] *J. Assoc. Official Agr. Chemists*, 1915, **1**: 154.
[2] *Z. Nahr. Genussm.*, 1908, **18**: 500.

percentage by weight may be calculated. Work has already been done along this line. Mr. Darling submitted the following:

In regard to determination of the volatile oil content of drugs and spices, it is believed that the following method will give accurate results with volatile oil content of 0.5 per cent and upwards, *i. e.*, aniseed, fennel, etc. The details were worked out in collaboration with Mr. Elgar O. Eaton.

Mix 10–25 grams of crushed seed with about an equal weight of sand. Place a pledget of cotton at the bottom of the inner tube of the Hortvet distilling apparatus. Introduce the prepared sample, tapping the tube gently, and cover with a pledget of cotton. Distil rapidly, using a condenser of the worm type. Collect the distillate in a flask having a graduated neck. When the receiving flask is nearly full, add sufficient pure salt to saturate the lower layer and read the volume of oil. In case the oil collects in small drops on the neck of the flask, it may be washed down with a little ether, and the ether removed by immersing the flask in the steam bath for a short time. The method is very rapid. With 10 grams of seed, practically all the oil comes over in the first 100 mils. It would conduce to greater accuracy if 25 grams of the sample were used, and a receiving flask of 200 mils capacity with neck graduated to 0.05 mils. We have been obliged to use the cassia flask which holds only about 100 mils.

In a conference the associate referee suggested some modifications. The results of our attempts, as outlined, will be discussed later.

PART III.

A considerable number of crude drugs or spices has been offered for entry in this country in an adulterated or otherwise objectionable condition. The work on the identification of new substitutes has been especially difficult on account of the frequent lack of information or authentic samples.

Striking examples of substitution or adulteration were the importation of Spanish digitalis (*Digitalis thapsi*), a non-official species, neither chemically nor pharmacologically known; the importation of mustard substitutes, such as Chinese colza, and Indian tori, for genuine mustards; of bitter fennel (*Foeniculum piperitum*) for the usual product, *Foeniculum capillaceum.*

Samples submitted as ipecac were found to be obtained from other species not containing any alkaloid. Especially serious were the two following findings: Senna leaves containing 20 per cent or more of *Tephrosia* leaves, used as fish poison, yielding the bitter glucoside tephrosin; marjoram leaves with about 10 per cent of *Coriaria myrtifolia* leaves, which contain a poisonous substance acting similarly to picrotoxin.

RECOMMENDATIONS.

It is recommended—

(1) That work on the method for the determination of volatile oil of mustards and mustard substitutes be continued.

(2) That work on the determination of ethereal oil in drugs and spices be continued.

REPORT ON PAPAIN.

By V. K. Chesnut (Bureau of Chemistry, Washington, D. C.),
Associate Referee on Pepsin and Papain.

The work on pepsin and papain was limited to investigations with papaya latex, mostly collected personally by the associate referee from papaya (*Carica papaya*) trees under cultivation chiefly at the Sub-tropical Experiment Station of the Office of Foreign Seed and Plant Introduction, at Miami, Florida. Dr. David G. Fairchild, in charge of the plant introduction work of the Department of Agriculture, generously consented to let the Bureau of Chemistry take samples from a portion of the fruits on each of all the varieties introduced there from all parts of the tropics, and also placed the Sub-tropical Laboratory at our disposal for drying the material. Forty-eight different samples were procured and dried as rapidly as possible over calcium chlorid in a box, through which air, heated by electricity to about 50°C., ascended. These samples, together with a composite, slowly sun-dried specimen collected at Miami by Dr. H. H. Rusby, nineteen procured from Professor J. E. Higgins, horticulturist of the Hawaiian Experiment Station, a few other genuine samples obtained by the associate referee from fruit grown under glass at Washington, and various commercial brands and imports furnished the material from which the data included in this report were obtained.

Papaya latex and papain, the partially purified product, are greatly misunderstood commodities. No attempt will be made to define either for this paper deals more particularly with the assay of dried latex. It must be borne in mind that "papaya latex" is not "papaya juice", as it is often erroneously called. It is not obtained from the crushed fruit, which contains considerable sugar and little or no proteolytic enzym, but from the milky sap which gushes chiefly from the rind of the unripe fruit, and also in very small quantity from the surface of leaves and stems when punctured. It contains little, if any, sugar. It was found on observation that the character of this latex varied a great deal, depending upon the ripeness and size of the fruit, whether collected at once when punctured, or after a few minutes, and especially if gathered an hour or so after bleeding, or after a drizzling rain. In most cases the latex, gathered without contact with iron, was nearly white, but occasionally it was brownish or nearly black when drawn, and twice no latex whatever was obtained on puncturing the unripe fruit. The ripe fruit yields a small quantity of a viscous solution which is not milky and is nearly devoid of proteolytic activity. The latex of young fruits coagulates very completely and very quickly, that from fully developed unripe fruits coagulates less completely and much more slowly. The latex

which gradually exudes and dries upon fruit, from which one portion of latex has been collected, is generally of a slightly brownish color and a little gummy. The chief quantity of latex was obtained in every case from the freshly punctured rind of fully developed but unripe fruits, and this should most fully represent the commercial article to which a definition of papaya latex should apply. Still, the other forms of the latex can not be excluded until further field and laboratory studies are made of them. In general, however, it may be said that good papaya latex is always easily friable between the fingers and possesses little or no offensive odor. All of the writer's samples were easily powdered and free from offensive odor, but nearly all were selected to represent chiefly fruit of medium size ranging down in greater or less number in different trees to the very youngest fruits. The largest fruits, though unripe, were left to mature. The writer was not then aware that the latex from young fruits was not very active, and wished particularly to study the latex of different horticultural varieties. His samples are, therefore, not strictly comparable for variety tests. The easy friability of the genuine latex permits one readily to distinguish the genuine from many of the hard, horny samples recently imported into the United States. These contained such a large quantity, often over half, of rice starch or bread stuffs, etc., that the importers, in order to have them admitted into the country, were compelled to relabel them in various ways so as plainly to indicate their approximate content of starch.

This form of adulteration is the most common, but fortunately it is the most easily handled, for it has been found that there is practically no starch or sugar in the genuine latex. Papain is also sometimes vile smelling, indicating autolysis or bacterial or fungus decay due to slow and perhaps dangerously insanitary drying[1]. Such samples are of low activity, but occasionally samples are received, especially in interstate commerce, that are considerably more active than are those usually imported. In some of these cases the product was found to be adulterated with milk sugar and pepsin.

Various methods have been suggested for the assay of papain, but few appear to have been based upon genuine samples, and none take proper cognizance of possible adulteration with pepsin, trypsin, and other lesser known proteoclastic and peptoclastic enzyms. It was found that several of the methods proposed did not exclude adulteration with pepsin and others did not exclude adulteration with trypsin or erepsin. The ordinary alkaline[2] method by digesting 8 grams of egg or fibrin in 100 cc. of water made slightly alkaline, upon which the commercial standard of 1 to 80 was adopted for papaya latex, was found to work quite as well with

[1] H. Huybertsz. *Chemist and Druggist*, 1916, **88**: No. 1897, 51.
[2] Real-Enzyklopädie der gesamten Pharmazie. Zweite Aufl., 1908, **10**: 4.

trypsin, only 100 to 200 mg. of one of the best brands being required for the purpose. Trypsin adulteration not excluded under this method would perhaps be unprofitable even at three or four dollars per pound for the latex on account of the high price of trypsin; but if, for example, the Shelley[1] modification of Sörensen's method of assay were accepted as official for papaya latex without qualifying tests, it would permit very gross adulteration with pancreatin or trypsin, because, as the author shows, good pancreatin can liberate from casein eight times as much amino acid as papaya latex, and do the work in only one-quarter of the time. It is, therefore, very evident that it is important first to decide upon what should be measured, and then to make sure by qualitative tests that other enzyms do not furnish the measurement observed. Adulteration with starch can be detected quickly by its reaction with iodin, but it is manifestly impossible in a product which differs in its physical properties so widely as does this latex for one easily to detect all possible forms of adulteration. Papaya latex should, therefore, be purchased wholly upon the basis of the extent of its characteristic proteolytic action.

What is the characteristic activity of papain? What is the power which we should measure, and upon what protein, if any, is its action most characteristic? Is its chief value in internal use, in the preparation of meat extracts[2], or the clarification of beer[3]? Papain can split up one and the same protein in a variety of ways in varying periods of time according to the temperature, the hydrogen-ion concentration and the presence or absence of other substances. As shown by Mendel and Blood[4] and verified by the writer, this is especially the case with prussic acid. It exerts a strong influence in shortening the time, as well as in increasing the depth, of cleavage. The reason for this is still unknown. Several such problems are at present unsolved, so we must be content with measuring some one characteristic action which may be definitely expressed in mathematical terms.

A comprehensive review of recent literature indicated that uncoagulated casein is the most generally satisfactory protein for comparing the action of various proteolytic enzyms at various hydrogen-ion concentrations. Its composition, especially its acid value when purified by the Hammarsten method, is nearly constant, and it is, therefore, an excellent material with which to make up solutions to a fairly definite hydrogen-ion concentration from a standard stock of casein by dissolving in standard sodium hydroxid and adding standard hydrochloric acid. It is also generally available at a fair price, and may be made quite readily in the

[1] *Analyst*, 1914, **39**: 170.
[2] Barral. *J. pharm. chimie* 1905, **22**: 395.
[3] Letters Patent. 1911, Nos. 995820 and 995824.
[4] *J. Biol. Chem.*, 1910, **8**: 177.

laboratory. Its chemistry is as well known as is that of most of th proteins. Furthermore, it is perhaps the most representative protei food and contains considerable amounts of the lysine and tryptophan groups necessary for growth. It has been shown that papain has quick digestive action on casein similar to that of trypsin and erepsin Casein was especially recommended by Hedin[1] for use in assayin trypsin. Scheermesser[2] states that casein is good for pepsin assay, bu not for trypsin. Neun[3] concludes that casein is good for the qualitativ testing of both pepsin and trypsin and is much better than egg for thi purpose. She also favors it somewhat for assay work but was unabl to get strictly quantitative results. Bogdandy[4], Shelley and Pratt[5] a used casein in their work.

A very great variety of modern assay methods, comparative, gravi metric, chemical, involving the determination of amino acid nitroge and its ratio to total nitrogen, bromin absorption values, etc., an physico-chemical methods, involving the use of the polariscope, colori meter, viscosimeter, refractometer, etc., were open for consideration i connection with the use of casein. The polariscope type of assay t which Fischer and Abderhalden[6] have paid much attention, especiall in connection with their enzym work with the polypeptids, and which moreover, has been worked out for pepsin in detail by Bogdandy, wa finally selected as the most expeditious and best suitable in every way fo the numerous assays involved. Assays with a gram of casein, as shown b Pratt, require only 10 mg. of the latex. This was a very valuable con sideration in this work, for there were only a few hundred milligram of some of the samples of latex. The possibility, in the use of such sma quantities, in favoring breeding investigations with a view to improvin the quality and quantity of papaya latex produced should be considere very especially in connection with this method. It is more reliable tha gravimetric methods for, aside from the mere solution effect, it has bee noticed that in papain digestion there is a certain amount of cleavag into simpler forms, including the more or less complex polypeptids an perhaps amino acids which can not be easily measured by the balance The same objection applies to the alkaline[7] assay with fibrin or whit of egg—it measures only the solution effect. The chief objection to thi method, however, is the main objection to all of the methods thus fa proposed—the indefiniteness of the hydrogen-ion concentration of th

[1] *J. Physiol.*, 1905, **32**: 468.
[2] *Apoth. Ztg.*, 1913, **28**: 752.
[3] D. E. Neun. An Examination of Certain Methods for the Study of Proteolyti Action. Dissert. Columbia Univ., 1915, p. 39.
[4] *Z. physiol. Chem.*, 1913, **84**: 18.
[5] *Philippine J. Sci.*, 1915, **10**: 1.
[6] Uber das Verhalten verschiedener Polypeptide gegen Pankreassaft und Magensaft— in Unterss. über Aminosäuren Polypeptide u. Proteine. 1899–1906. p. 595.
[7] Real-Enzyklopädie der gesamten Pharmazie. Zweite Aufl. 1908, **10**: 4.

substrats used. This investigation has shown that considerable care must be taken, not so much to the acidity as to the hydrogen-ion concentration of the substrat. Papain has a comparatively narrow zone of activity. The method under consideration does not establish any definite amount of alkali to be added to the fibrin or egg and, therefore, no exact or even comparative measurement of activity is possible with it. Indeed, the method has, through this neglect, led to at least one report of total inactivity, whereas, as a matter of fact, the sample in question was found by the associate referee's method to be an excellent latex with no enzym adulterant. Attention has been called to the fact that the Shelley method would permit gross adulteration with trypsin. It is believed that this is due largely to the unfavorable alkalinity of the casein solution used. This criticism may apply to Neun's work, but in her polariscope work she used too large an amount of some of the enzyms, and should not have expected comparative results with limited quantities of casein. Pratt did considerable work to show how narrow is the zone of papain activity, but adopted in his report the acidity of some unnamed commercial brand of sweetened condensed milk. It is conceivable that this acidity may vary considerably with different brands, especially in any that might be made of milk of questionable age. Perhaps ordinary casein is open to the same criticism, but the acidity of the uncoagulated casein, prepared by the Hammarsten process, has a fairly definite acid value. From 8.3 to 8.7 cc. of N/10 sodium hydroxid are required in different samples to make 1 gram neutral to phenolphthalein. Three 1 pound samples of Hammarsten's casein were secured for this investigation and mixed intimately, by the use of a sieve, and the purity of the mixture determined from data given by Abderhalden[1].

In weighing out the casein for digestion experiments, due allowance was made for the moisture present by calculating the protein to the anhydrous basis. Standard carbon dioxid-free sodium hydroxid was prepared of N/5 strength by the Morey[2] method, using pure sublimed benzoic acid furnished by the Bureau of Standards, and this alkali was used in preparing standard hydrochloric acid.

Sixty cc. of N/5 sodium hydroxid were added to 12 grams of casein previously thoroughly shaken in a 300 cc. flask with about 100–150 cc. of water, and after vigorously shaking the mixture for about 30 minutes until the casein was dissolved, the flask was filled to the mark with water. Twenty-five cc. of this alkaline casein solution, to which 20 cc. of water were added, had a hydrogen-ion concentration of $P_H = 10^{-9.35}$, a point determined approximately by the substrat turning very light blue with thymolphthalein. This figure was determined by Mr. G. H. Mains of

[1] Bio. chem. Handlexikon, 1910–11, **4**: 105.
[2] U. S. Bur. Standards Bull. **8**: 643.

the Physical Chemistry Laboratory of the Bureau of Chemistry, and is the basal solution from which all substrats were derived by addition to separate 25 cc. portions in 100 cc. measuring flasks of varying amounts of water and of the standard acid or alkali, leaving a final volume of 45 cc. before the addition of the constant volume of 5 cc. adopted for the papain and other digestion solutions. The hydrogen-ion concentrations of all these various 45 cc. substrats have not yet been determined, but the solution found by the associate referee to be optimal for papain, the substitution in the basal solution of 2.5 cc. of N/5 hydrochloric acid for 2.5 cc. of water, was found by Mr. Mains to be $P_H = 10^{-6.21}$. The extent of activity was found to vary only a little when from 2 to 4 cc. of the N/5 hydrochloric acid were substituted for the same quantity of water. The activity drops off very rapidly if less than 2 cc. are added; less rapidly if more than 4 cc. are added. The substitution of 5 cc. of the acid for 5 cc. of water causes strong coagulation of the casein, but a 12.5 cc. substitution gives a clear solution which is about optimal for pepsin. The optimal zone for papain may be fairly well determined with indicators. The 45 cc. solution to which the very slightly acid papain solution is added should be basic to methyl red and phenolsulphonephthalein and acid to paranitrophenol and phenolphthalein.

The substrats in the 100 cc. measuring flasks referred to above were placed in a water bath held constant at 37.5° C. for about 30 minutes while the solution of the latex or enzym under examination was being prepared. Water and 1 per cent sodium chlorid solution, both with and without toluene, were tried as solvents, but 1 per cent sodium chlorid solution without toluene was found best. One hundred and fifty mg. were ample material for acidity determinations and for eleven assays. This was placed in 75 cc. of 1 per cent sodium chlorid and digested with occasional agitation at room temperature for 30 minutes. It was then filtered rapidly through a folded filter, transferred to a burette and added in 5 cc. portions, representing 10 mg. of latex, to the warmed substrats, which were then replaced in the bath and digested exactly 30 minutes. They were then removed and to each was added immediately 30 cc. of the Bogdandy precipitating mixture (consisting of 132 grams of anhydrous sodium sulphate, 100 grams of magnesium sulphate and 200 cc. of 95 per cent alcohol diluted up to 2000 cc. with water), and 5 cc. of N/1 hydrochloric acid. The mixture and the acid were previously measured out in flasks so that they could be added quickly. The flasks were cooled to 20°C. and water added to the 100 cc. mark. The flasks were well shaken, the contents filtered and readings made with the filtrates at 17°C. in 200 mm. tubes in a S. & H. half-shadow polariscope, by means of which the angular rotation could be read accurately to within 0.01° or 0.02°. No difficulty was experienced in obtaining clear filtrates

except in the case of the most active samples. These had to be filtered repeatedly through double filters.

Many samples of latex prepared in various ways from all available varieties of fruit in all stages of growth were tested at from 3 to 11 different hydrogen-ion concentrations, but the maximum effect was invariably obtained when the enzym was added to the 45 cc. substrat, the hydrogen-ion concentration of which was $P_H = 10^{-6.21}$. The samples thus tested included, among others, latexes produced naturally from one year old trees in Florida, Honolulu, and Montserrat, and under glass at Washington, and one from the very small fruit of a tree several years old; those representing rapidly and slowly coagulating forms and coagulation residues, some of recent collection and some two to five years old, and one exposed to the air of the laboratory for nearly a year; those dried slowly and rapidly in the sun, at a moderate heat in a dryer and at a temperature a little below the boiling point of water. When the same samples were tested at the optimal hydrogen-ion concentration for pepsin, little or no activity was shown, as was also the case when tested at the optimum for trypsin. Very considerable activity was shown, however, both by trypsin and by papaya latex at a concentration about half way between their optimal points.

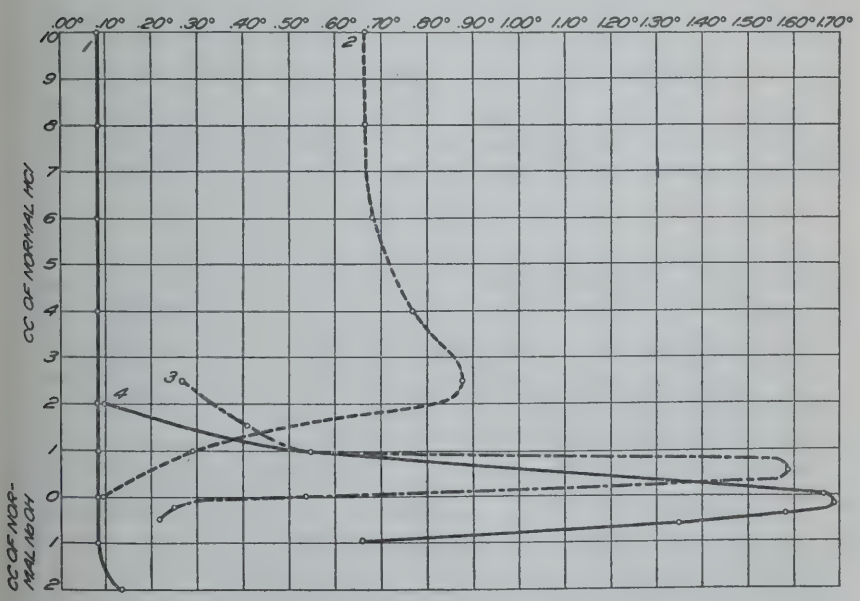


FIG. 1. Uncorrected curves showing influence of hydrogen-ion concentration upon 10 mg. enzym digestions of 1 gram of casein: 1. Correction curve; 2. U. S. P. scale pepsin; 3. Best papaya latex, Inv. No. 4934; 4. One of the best brands of trypsin. Thirty minute digestions at 37°C.

Figure 1 furnishes a detailed sketch of the work of these three enzyms and gives a correction curve, No. 1, showing the amount of rotation found when 5 cc. portions of water are substituted for the enzym solution and the assays carried out in the same manner as the enzym assays. Five cc. of an aqueous solution of 10 mg. of the enzym were added in each case to substrats containing exactly 1 gram of anhydrous casein, and the digestion carried on 30 minutes at 37.5°C. The abscissæ

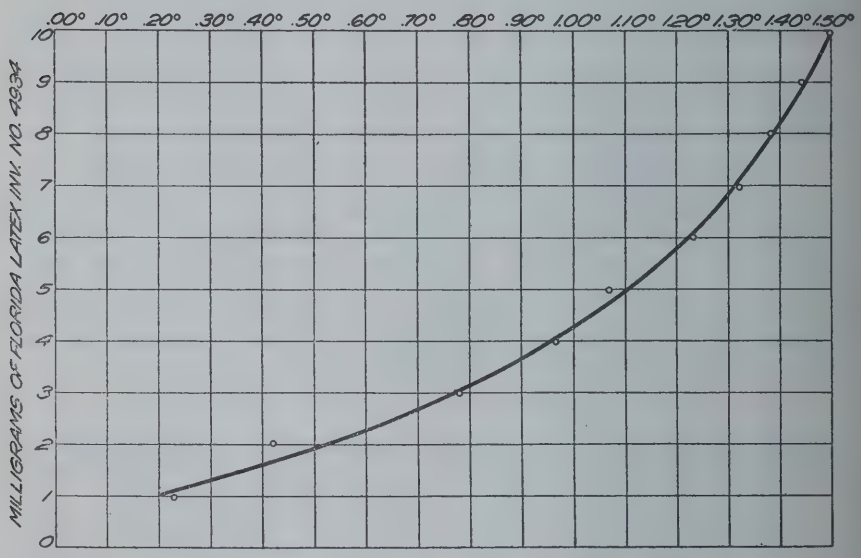


FIG. 2. Corrected curve showing negative-rotation effect of different quantities of latex, Inv. No. 4934, upon 1 gram of casein at the optimal hydrogen-ion concentration. Thirty minute digestions at 37°C.

represent the number of cc. of hydrochloric acid, or of sodium hydroxid, added to the basal solution to bring the volume up to 45 cc. after addition of water; the ordinates represent the negative polariscopic reading at 17°C. of the filtrates from the digestion mixtures after precipitation by the Bogdandy mixture and dilution to 100 cc. The actual points of observation are indicated by dots. Scale pepsin of U. S. P. value was used for Curve No. 2, and one of the best commercial brands of trypsin for Curve No. 4. The points for Curve No. 3 were furnished by Florida latex, Investigation No. 4934, obtained by drying the juice at about 50°C. over calcium chlorid. It is characteristic of all of the many samples examined that the highest point of all the curves was invariably at the hydrogen-ion concentration here shown as the optimum and that the curves descend very rapidly on both the acid and alkaline sides. This

latex was the most active one examined, but the best Hawaiian sample was little, if any, inferior. Some samples were so nearly worthless that the maximum rotation found was very low, as was the case with the five year old Hawaiian sample, Informal X, I. S. No. 8019-K, the reading for which was −0.13°. The average reading found in the case of the Florida samples was 0.54°; that for the eighteen Hawaiian samples, 0.80°. These figures, however, can not in any way be regarded as showing the comparative activity of the latex from the two places. Had the latex of selective individual fruits been compared, very much higher averages would have been found in both cases. Variety tests for comparative yield and activity must be carried out only with latex from fully developed but unripe fruit.

In Figure 2 the ordinates show the negative rotation at 17°C. as above, but in this case the abscissæ represent the quantity in milligrams of latex No. 4934 added to the ten substrats, which were in every case of the optimal hydrogen-ion concentration. Nine-hundredths of a degree was subtracted in each case from the observed reading, so that comparison may be made at once with the change in deviation furnished by any 10 mg. sample of latex and a close estimate be made of its comparative strength. If sample No. 4934 were rated at 100 per cent, a net change in rotation of 1.07° caused by any 10 mg. sample would indicate that the sample is of 50 per cent strength.

The curve found is not an altogether perfect one, but it is believed to be very serviceable for papaya latex work. A study of the two figures will show how easily enzym adulteration may be detected and the papain value of any spurious sample of latex may be determined from a few polarimetric readings. For the detection of possible adulteration with trypsin, the polarimetric results must be supplemented with qualitative tests.

No gravimetric determinations were made to show the comparative amount of undigested protein after 30 minutes' digestion at the optimal acidity for different samples, but simple inspection in a great many cases showed that there was a general parallelism, especially in the weaker latexes, with the results of polarimetric observation. But with the full 10 mg. amounts of the best samples, the parallelism ceased. Considerably greater deviation was noted in 8 to 10 mg. quantities after apparent solution had nearly ended.

The measurement of enzymic activity will always be somewhat intangible until we have a more complete knowledge of the structure of the protein molecule. If we conceive it to be made up of a complex aggregation of polypeptid linkages, as it apparently seems to be, it would undoubtedly be better to measure the extent of proteolytic action by

the ratio of amino nitrogen found at any one time, not to the total nitrogen, but to the total amino nitrogen found upon complete hydrolysis.

Sörensen[1] was the first to propose the formalin method of measuring this action, but several methods of making the same determination have more recently been advanced. Of all these, the Sörensen and the Van Slyke[2] methods were tested out to a limited extent. Dr. J. F. Brewster of the Bureau of Chemistry kindly made a Van Slyke determination for the writer, but difficulty was encountered in the profuse frothing of the reaction. It requires very much more time than the polariscopic method and was consequently abandoned. The Sörensen method was not adopted for the same reason.

The method here given is a comparatively simple one, very well adapted for research and seems well adapted for the assay of papain, especially where adulteration with other enzyms is suspected. It is hardly possible for any proteolytic enzym to show no activity in substrats with the eleven hydrogen-ion concentrations selected. In practice the field can be amply covered by three assays made at the optimum for pepsin, trypsin and papain, respectively. Pepsin is the only enzym adulterant which has been reported in papaya latex and in papain, and the method of itself serves admirably to indicate its presence. If further tests be needed to detect pepsin or trypsin, the following will be of service.

The presence of trypsin may readily be detected by the very great ease with which it breaks up glycyl-l-tyrosine ("peptone Roche") with the formation of the very characteristic and easily recognizable bundles of needle-shaped crystals of tyrosine[3].

To 0.2 gram of this di-peptid add 5 cc. of a freshly prepared and filtered solution made by digesting 5 grams of the latex 30 minutes at 37°C. in 25 cc. of water to which 1 cc. of N/1 potassium hydroxid has been added. Add 2 drops of toluene, stopper loosely and digest at 37°C. If trypsin or certain peptoclastic enzyms are present, the crystals of tyrosine will generally appear after 8 to 24 hours' digestion. The high price of trypsin will militate against its use to increase the activity of any but the poorer grades of papain, for which a high price is demanded. Papain also separates tyrosine from glycyl-l-tyrosine, but only in very minute quantities.

The rapid, 80–90°C., digestion[4] by papain of a solution of raw egg albumen in water slightly acidulated with acetic acid is shared, so far as known, only by bromelin, which is probably not used as an adulterant of papain. The digestion mixture is brought to the boiling temperature in a test tube within a couple of minutes and the biuret reaction is then

[1] *Biochem. Z.*, 1907, **7**: 45.
[2] Proc. Soc. Exp. Biol. Med., 1910, **7**: 46.
[3] L. Michaelis. In Abderhalden's Handb. der Biochem. Arb. Methoden. 1910, **3**: 21.
[4] *Soc. de Biol.*, 1906, **60**: 309.

applied to the filtrate. A strong pink color is produced if papain is present. It must be remembered, however, that unless especially prepared, pepsin contains peptones. Another high temperature test of great historic and practical interest is a modification of a very simple experiment originally made by Roy[1], one of the first investigators of the latex. To a single 10 gram piece of tough beef immersed in 25 cc. of water, held at 75–80°C., add a half gram of powdered latex. The beef is reduced almost to soup within 15 minutes by a good latex, but is unchanged by a like weight of either pepsin or trypsin.

The meeting adjourned at 4.15 p. m. for the day.

---

[1] *J. Med. Chirug. Pharmacologie*, 1874, **59**: 252.

SECOND DAY.

TUESDAY—MORNING SESSION.

REPORT ON FOOD ADULTERATION.

By Julius Hortvet (Dairy and Food Department, St. Paul, Minn.), *Referee.*

It is a satisfaction to note among the referee reports of the past two years not only a widening of our field of study of analytical methods of procedure, but also a reaching out into subjects relating more than heretofore to basic principles underlying the science of modern chemistry. We are not unaware of the advances which have been made from the more or less purely empirical methods which constituted in large measure our great reliance not many years ago. As a conspicuous case in point, the application of methods of study following mainly theoretical lines has resulted in an entire rearrangement of the chapter on coloring matters in our revision of official methods of analysis. Take also as illustrations the referee reports on fruit products, dealing with a collaborative study of methods for the quantitative determination of the common fruit acids; investigations taken up on baking chemicals, involving not only ordinary methods of analytical procedure, but also suggesting the application of principles of physical chemistry hitherto seldom enlisted in our attempts to overcome difficulties; and the plan of work demanded as a result of recent advances in the technology of edible oils and fats. There is no doubting the fact, and this point must be kept ever plainly before us, that we have recently arrived at a critical turning point or at a point of greatly increased impetus in the forward movement of that branch of applied chemistry dealing with the analysis of food products and methods of detecting adulteration.

In line with this brief statement of facts intended to describe, in a general way at least, the conditions under which we are laboring, it seems necessary to speak a word relative to the subject titles which have been announced in the programs of our meetings for two or three years past. Considering the state to which we have actually advanced in our work, it is clearly apparent, in a number of instances at least, that our present subject titles are seriously in need of revision, and that there is also doubtless a call for the addition to our program of a number of subjects hitherto not taken up in connection with our collaborative work. In the first place, a clearer distinction should be made in the matter of subject headings between those lines of investigation which

are of special interest to those chemists engaged in experiment station work, or work relating chiefly or wholly to agriculture or dairying, and those lines of investigation which are related entirely to the general subject of food analysis and methods designed for the purpose of detecting food adulteration.

On examining the program we find that the subject, dairy products, appears in two places and is handled by two separate referees. A distinction in title should be made between these two subjects, inasmuch as it is obvious that the two lines of investigation have not a common purpose in view. The work on dairy products, which relates primarily to experiment station work or has to do with special problems not in any way essentially connected with the work relating to food adulteration, may be continued under its present title, viz., dairy products; and by way of differentiating in a matter where a real distinction certainly exists, it is therefore suggested that the present title, dairy products, under food adulteration, be changed to read "Milk and Milk Products". In the same manner, we already have a fair distinction between the subject, sugar, which appears on the general program of the first day, and the subject, saccharine products, which occurs in the group under the heading "Food Adulteration".

This plan of differentiating one class of work from the other is carried out apparently well enough in the present arrangement of program and no further suggestions on this particular point seem to be necessary. Under the general subject, food adulteration, however, there is clearly a call for further revision in the matter of subject titles. The associate referee on cocoa and cocoa products has very properly recommended and urged that this subject be changed so as to read "Cacao Products". A thorough examination into the origin and meaning of these terms will reveal the necessity for such a change. Also, along the line of broadening our work as well as in harmony with our plans to intensify, it is suggested that the title, flavoring extracts, be changed so as to read "Flavoring Extracts and Essential Oils"; that the title, spices, be broadened to read "Condiments and Spices"; that the title, baking powder, be changed to "Baking Powder and Baking Chemicals"; that the subject, beer, be broadened so as to read "Malt Liquors and Beer"; and that the subject, wine, be expanded into the subject "Fermented Fruit Juices, Wines and Ciders".

Other changes, though probably of minor importance, may be suggested, especially in view of the fact that food control work has recently been extended into a good many classes of products not heretofore seriously taken into consideration. We find ourselves in recent years dealing more and more with crude materials, the original natural products from which manufactured products are derived. Along this line it is

proposed that we expand the subject, colors, to "Colors and Commercial Dyestuffs"; cereal products to "Cereals and Cereal Products"; fruit products to "Fruits and Fruit Products"; and that the subject, vegetables, be enlarged to "Vegetables and Vegetable Products". Relative to the subject, meat and fish, it is apparent that a fictitious distinction has inadvertently been made between the meanings of two terms of common usage. Doubtless there may be individuals who make a certain distinction between meat and fish; nevertheless, in harmony with the purposes and plan of our work, it is recommended that this subject be changed so as to read "Meat and Meat Products".

In the above list of revised titles the further recommendation is made that we include two additional subjects under the respective headings "Confectionery" and "Soft Drinks". These recommendations are offered in the belief that they are in the main timely, and it is therefore urged that this matter be taken up for consideration by the appropriate committee having in charge the recommendations of referees.

REPORT ON COLORS[1].

By W. E. MATHEWSON (Bureau of Chemistry, Washington, D. C.),
Associate Referee.

Chapter XXVIII of the official methods[2], which has not been changed for a number of years, was thoroughly revised by the Committee on Editing Methods of Analysis. It seemed that the tentative methods should be brought before the association for criticism this year, and with this in view copies of the draft were sent to the chemists collaborating on the color work. It was suggested to the collaborators that they make a few mixtures from food products and colors that chanced to be of special interest to them, try the methods on these, and report criticisms to the association. In addition, it was hoped that some advance might be made in the selection of methods for the natural coloring matters. However, little was attempted or accomplished in this field[3].

The statements of the collaborators follow. Mr. L. A. Salinger (U. S. Food and Drug Inspection Station, U. S. Custom House, Savannah, Ga.), who made a very complete examination of the methods, has abstracted his full report.

---

[1] Abstract.

[2] U. S. Bur. Chem. Bull. **107**, rev.: 190.

[3] L. S. Palmer and W. E. Thrun have recently published a paper (*J. Ind. Eng. Chem.*, 1916, **8**: 614) discussing the detection of natural and artificial coloring matters in oleomargarine and butter. They conclude that it is not possible to distinguish added carrotin from that naturally occurring in the fat.

L. A. Salinger.—The separation of the eight permitted coal tar colors by immiscible solvents was selected from the work outlined by the association. In this separation I used aqueous solutions and solutions of food products that were freed from alcohol by evaporation, adding one-half volume concentrated hydrochloric acid and extracting the color by amyl alcohol and washing out the color from the amyl alcohol as outlined in the procedure, using N/4 hydrochloric acid in the first washings. In order to make the behavior of the colors comparable, all the extractions and washings were made in the same way. The procedure was tried first on a mixture of the eight permitted colors; then combinations were made with different food products, including cordials, grapefruit, marmalade, etc. From all these extractions the colors were separated and were properly identified by the test on wool, matched against standard colors. One fractionation was sufficient, especially if the first and last washings of each group were rejected.

In separating Naphthol Yellow S and Ponceau 3 R from each other, it was found that they were completely separated by adding salt to saturation. This is more complete than the ethyl acetate separation. The Naphthol Yellow S does not dye readily from this strong salt solution. It is best to take out the color with acid amyl alcohol. Then the wool will dye readily in the aqueous washing.

Tartrazine, Indigo Carmin and Amaranth were easily separated from each other by means of sodium hydrosulphite. Other reagents were tried, but were not successful. In washing out Erythrosin from Orange I, it is best to use distilled water. Our tap water was alkaline enough to wash out the Erythrosin completely in two washings.

My idea of the description of the colors produced by the various reagents of the eight permitted colors dyed on the cloth tallied very closely with that described in the procedure. I should say the scheme outlined in the procedure will give satisfactory results with any person using ordinary care in following out the instructions. By refractionation and using definite amounts of solutions, reagents and number of times of washing, the groups can be completely separated and entirely freed from each other. especially if the first and last washing in each group is rejected.

C. L. Black (*U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, Philadelphia, Pa.*).—I have made a very critical study of the methods submitted for the association work, and have also tested them in various ways in which I would expect defects to show up, and have found them quite satisfactory. I feel that the greatest mistake in these methods lies in failure to caution the analyst as to the separation of colors not being sharp and not to use the portions obtained by the final extractions with one strength acid in his identification of the color extracted with that acid. I made a number of individual tests and found that a mixture of the permitted colors was separated and identified with ease, using the above caution. Then to a mixture of the permitted colors, with the exception of the blue and green, I added Martius Yellow, S. & J. No. 3, and found no interference. To a similar mixture Coccine, S. & J. No. 106, was added and appeared with the Amaranth, from which I know of no way to separate it; Orange II, when added, appears as a contamination of the Erythrosin.

For some time the following test for Erythrosin has been used in this laboratory: A small amount of the dyestuff is obtained by stripping the dyed fiber and evaporating in a porcelain dish. A beaker (which will fit inside the porcelain dish) is then prepared containing ice-water and a lump of ice and on the bottom outside a drop of starch paste. Sulphuric acid is then added to the dyestuff in the dish, the beaker placed over it and the dish heated on a wire gauze, liberating iodin, which is shown on the drop of starch paste.

On the whole, I feel that there is no method of separating dyes so satisfactory as by using a chart on the solubility of dyestuffs in various organic solvents when shaken with acids, etc. Then, by starting at the highest strength acids and coming on down the

list, the analyst can see so much more easily what dyes it is possible he may be extracting at any point. If such a chart could be made sufficiently complete to cover practically any possible color encountered, the analyst would need nothing but it and his table of reactions of dyed fibers and a few specific chemical tests which are known for various dyestuffs.

No work on the natural colors was reported this year by collaborators.

TARTRAZINE[1].

By AIDA M. DOYLE[2] (Bureau of Chemistry, Washington, D. C.).

Short reference was made to the reasons why an additional yellow color for foodstuffs was needed and to the action of the Department of Agriculture in issuing Food Inspection Decision 164 permitting the use of tartrazine. The components, methods of manufacture and constitution of the dye were briefly discussed and illustrated. As an aid in the understanding of the properties of the dye, brief reference was made to the uses of tartrazine and other pyrazolon dyes in the industries, special emphasis being laid on the structure as it affects the tests for identification.

A number of identification tests for tartrazine, on the dry dye, the solution 1 to 1000 in water and the dyed fiber, were described and compared with those applied to Naphthol Yellow S, mimeograph copies of some of the more distinctive tests being supplied. Methods of separation of the color from the foods themselves, particularly paste products, were suggested and a number of illustrative samples shown.

No report was made on saccharine products, as there was no associate referee on this subject.

REPORT ON FRUIT PRODUCTS.

By P. B. DUNBAR[3] and H. A. LEPPER (Bureau of Chemistry, Washington, D. C.).

In accordance with the recommendations made in the last report on fruit products, the work has been confined to studies of the uranyl acetate method for the determination of malic acid and of the Kunz modification[4] of Stahre's method[5] for the determination of citric acid.

---

[1] Abstract.
[2] Present address, 1365 Oak Street, Washington, D. C.
[3] Associate referee.
[4] *Arch. Chem. Mikros.*, 1914, **7**: 285; *C. A.*, 1915, **9**: 687.
[5] *Nordisk Tidskrift*, 1895, **2**: 141; *Z. anal. Chem.*, 1897, **36**: 195.

MALIC ACID.

Three procedures for the determination of malic acid, adapted to various types of fruit products, have been devised. These are based on the polariscopic method proposed by Dunbar and Bacon[1] and embody a number of the suggestions made by the previous associate referee on fruit products, Mr. H. C. Gore[2]. For advice and assistance in devising these procedures, the writers are much indebted to Messrs A. F. Seeker and R. E. Doolittle. The malic acid methods are as follows:

1 *Method I.*

(For fruit juices and similar products which contain no tartaric acid and not over 15 per cent of sugars and in which the color does not interfere with polarization.)

Filter the sample, if necessary to secure a solution which can be polarized readily, and polarize, using a 200 mm. tube if possible.

If no free mineral acids are present, it is unnecessary to neutralize the sample before subjecting to the treatment which follows. If the sample contains free mineral acid, transfer a measured portion (75 cc. is a convenient volume) to a 100 cc. graduated flask; add enough standard alkali to neutralize the total acidity; dilute to the mark; mix well and filter.

Transfer 25 cc. of the sample, or of the neutralized solution, to a flask graduated to 25 and 27.5 cc.; add about 2.5 grams of powdered uranyl acetate and shake vigorously at frequent intervals for 3 hours, keeping the mixture well protected from light. If all of the uranyl acetate dissolves, more should be added and a small amount should remain undissolved at the end of 3 hours. Dilute the solution to the 27.5 cc. mark with saturated uranyl acetate solution; mix well and filter, if necessary. Polarize, if possible, in a 200 mm. (or longer) tube. If the solution is too dark to polarize in a 200 mm. tube, a 100 or 50 mm. tube may be used. Multiply the reading by 1.1 to correct for dilution and, if a neutralized solution was used, make a further correction for that dilution.

Multiply the algebraic difference in degrees Ventzke between the corrected readings, obtained before and after treatment with uranyl acetate, calculated to the basis of a 200 mm. tube, by the factor, 0.036, to obtain the weight of malic acid in the sample in grams per 100 cc.

Make all polarizations at room temperature with white light, taking care that all solutions are polarized at the same temperature. Make at least 6 readings in each case and take an average of these.

In the case of dark colored fruit juices which can not be polarized readily, approximately quantitative results may be obtained by adding to the solutions a few drops of bromin, shaking thoroughly and filtering just before polarization.

Method II.

(Approximate determination for fruit juices and similar products containing no tartaric acid and more than 15 per cent of sugars.)

2 PREPARATION OF SOLUTION.

Weigh out 25 grams of the sample and transfer to a 600 cc. beaker with a little 95% alcohol. Add alcohol, a little at a time, stirring the mixture well and warming, if

[1] U. S. Bur. Chem. Cir. 76.
[2] U. S. Bur. Chem. Bull. 162, 65; *J. Assoc. Official Agr. Chemists*, 1915, 1: 480.

necessary, to insure perfect solution of all alcohol-soluble substances, until 200 cc. have been added. Filter on a Büchner funnel, using suction, and thoroughly wash the precipitated pectins and insoluble matter with 95% alcohol. Disregard any slight turbidity which may appear in the filtrate when the washings are added. From the determination of total acidity, calculate the amount of N/4 barium hydroxid solution required nearly to neutralize the acidity in the 25 grams of sample taken. To the combined filtrate and washings in an Erlenmeyer flask, add the calculated quantity of barium hydroxid solution, stir until reaction is complete and then add 3–5 drops, or more if necessary, of an aqueous solution of barium acetate (50 grams in 100 cc.) to insure the presence of more than sufficient barium to combine with all the acid in the sample. Make up the volume of the mixture to about 375 cc. (not less) with alcohol, and reflux until the precipitate settles readily after being shaken. This may require 3–4 hours. Filter with suction and thoroughly wash the precipitate in the flask and on the paper with 95% alcohol. Transfer the portion on the filter quantitatively to the original flask, rinsing the paper with a jet of hot water for this purpose. Digest the precipitate with hot water, containing 2 grams of sodium sulphate in solution until the reaction is complete, and boil until the barium sulphate precipitate settles readily. Concentrate by evaporation, if necessary, and transfer quantitatively to a 100 cc. volumetric flask with a little hot water, cool, and make up to volume with water. Filter and treat portions of the filtrate as directed in **3**.

3 DETERMINATION.

Transfer 25 cc. of the solution, obtained as directed in **2**, to a volumetric flask graduated to 25 and 27.5 cc.; add about 2.5 grams of pulverized uranyl acetate and shake vigorously at frequent intervals for 3 hours, keeping the solution well protected from light. If all the uranyl acetate dissolves, more must be added in order that a small amount may remain undissolved at the end of 3 hours. Dilute the solution to the 27.5 cc. mark with a saturated uranyl acetate solution, mix well, filter if necessary, and polarize, using the same precautions as described in **1**. Multiply the reading by 1.1 to correct for the dilution.

Polarize another portion of the filtrate, obtained as directed under **2**, which has not been treated with uranyl acetate. Multiply the algebraic difference in degrees Ventzke between the two readings, calculated to the basis of a 200 mm. tube, by the factor, 0.036, to obtain the weight of malic acid in grams per 100 cc. in the solution as obtained in **2**.

Method III.

(Approximate determination for products containing tartaric acid.)

4 PREPARATION OF SOLUTION.

Prepare the sample as directed under **2**, up to the point of filtration and washing of the barium malate precipitate, then dry the precipitate thoroughly and transfer the portion on the filter quantitatively to the original flask, which has been previously dried, rinsing the paper with a jet of hot water for this purpose. Digest the precipitate with hot water, transfer quantitatively to a 100 cc. volumetric flask with a little hot water, cool, make up to volume with water and filter to remove undissolved barium tartrate. This amount of water is sufficient to dissolve barium malate up to amounts as large as approximately 0.9 gram. More than 100 cc. of water must be used when more than 0.9 gram of barium malate is present. The amount of barium tartrate dissolved by hot water is so small as to affect the polarization, after treatment with uranyl acetate, only to a slight extent.

5 DETERMINATION.

Proceed as directed in 3, using the solution prepared as directed in 4.

CITRIC ACID.

The Kunz-Stahre method for the determination of citric acid is essentially that given in the report of last year, although a number of minor changes have been made. It differs little from the method originally published by Kunz except for the fact that the citric acid is first precipitated as barium citrate.

Quantitative Determination.

(Applicable in the presence of sugar and malic and tartaric acids.)

1 REAGENTS.

(a) *Barium hydroxid solution.*—Approximately N/4.

(b) *Barium acetate solution.*—Fifty grams of barium acetate in 100 cc. of water.

(c) *Dilute sulphuric acid.*—Equal volumes of sulphuric acid and water; also one volume of sulphuric acid and five of water.

(d) *Potassium bromid solution.*—Fifteen grams of potassium bromid in 40 cc. of water. A solution of sodium bromid (16 grams in 50 cc. of water) may be substituted for the potassium bromid solution.

(e) *Potassium permanganate solution.*—Five grams of potassium permanganate in 100 cc. of water.

(f) *Ferrous sulphate solution.*—Twenty grams of ferrous sulphate in 100 cc. of water containing 1 cc. of concentrated sulphuric acid.

2 DETERMINATION.

Proceed as described under "Malic Acid, 2," to the point where the precipitated barium salts are washed and transferred to the original flask. Transfer the precipitate quantitatively from the filter to the flask with a jet of hot water; boil until alcohol can no longer be detected by odor and add enough dilute sulphuric acid (1 to 5) to precipitate all the barium originally added and to allow 2 cc. in excess. Evaporate by careful boiling to a volume of 60–70 cc., cool and add 5 cc. of freshly prepared saturated bromin water, or enough to show a distinct excess. Transfer quantitatively to a 100 cc. volumetric flask, with water, and dilute to the mark at standard temperature with water. Mix thoroughly, allow the precipitate to settle and filter through a dry paper. The precipitate may be separated by centrifugalizing and the supernatant liquid decanted, if necessary. Pipette an aliquot portion of the filtrate, containing not more than 400 mg. of citric acid (calculated from the total acidity of the sample), into a 300 cc. Erlenmeyer flask. The amount of the citric acid in the aliquot should, if possible, exceed 50 mg. Add 10 cc. of sulphuric acid (1 to 1) and 5 cc. of potassium bromid or sodium bromid solution, mix, warm the flask in a water bath to 48–50°C., and allow it to remain in the bath for 5 minutes. After removing from the bath, add 25 cc. of 5% potassium permanganate solution from a burette, in rapid drops, with frequent interruptions and constant, vigorous shaking, care being taken that the temperature during oxidation does not exceed 55°C. Set the flask aside until the hydrated peroxid of manganese begins to settle. The supernatant liquid should be dark brown, showing an excess of permanganate (if an excess is not indicated, add more perman-

ganate). Shake, again set aside to settle, and repeat this operation until the precipitate takes on a yellow color and most of it has dissolved. Finally, while the solution is still warm, remove the last undissolved portion of hydrated peroxid of manganese precipitate and also the excess of bromin by adding drop by drop a clear, concentrated solution of ferrous sulphate. Allow the solution to cool with occasional shaking. If the operations have been properly carried out, a heavy white precipitate of pentabromacetone is obtained which becomes crystalline on occasional shaking and, in this condition, is entirely insoluble in water. Allow the mixture to stand overnight, collect it by means of gentle suction in a porcelain Gooch crucible provided with a thin pad of asbestos, previously dried over sulphuric acid in a vacuum desiccator, wash with water slightly acidified with sulphuric acid and finally wash twice with water. Dry the precipitate to constant weight over sulphuric acid in a vacuum desiccator, protected from strong light. The weight of pentabromacetone multiplied by the factor 0.424, gives the equivalent weight of citric acid ($H_3C_6H_5O_7$). It sometimes happens that the pentabromacetone is first obtained in the form of oily droplets. These also become crystalline, on standing or on cooling, but are usually discolored by negligible traces of manganese or iron. The accuracy of the result is not vitiated when this occurs.

The above method may be applied directly to the sample under examination without previous precipitation of the citric acid as the barium salt when the amounts of sugars or other permanganate reducing substances are not excessive. In this case the determination should begin with the addition of 2 cc. of sulphuric acid (1 to 5) and saturated bromin water.

COLLABORATIVE WORK.

In the original publication[1] the most favorable limits of concentration for the malic acid method are given as between 0.2 and 2.5 per cent. Method I for the determination of malic acid in fruit juices and similar products containing not over 15 per cent of sugars and no interfering colors, is practically identical with the original method which was made the subject of collaborative work by the previous associate referee, Mr. Gore[2]. A sweet cider containing 0.50 per cent of free malic acid as determined by titration was sent out by him to eight collaborators. The results reported varied from 0.468 to 0.531 per cent and averaged 0.59 per cent of malic acid. These results were so satisfactory that it was not considered necessary to give Method I a further trial in the collaborative work this year.

The determination of malic acid in the presence of large amounts of sugars, or of tartaric acid as in Malic Acid Methods II and III, presents difficulties not encountered in ordinary fruit juices. In order that these procedures might be given a severe test, it was thought advisable to prepare samples of jelly containing known amounts of malic as well as citric acid, and in some cases tartaric acid, for analysis by the collaborators.

Numerous determinations of citric acid in aqueous solutions and in fruit juices were tabulated in last year's report and the results indicated

[1] U. S. Bur. Chem. Circ. **76:**
[2] U. S. Bur. Chem. Bull. **162:** 63.

that the method could be applied to these products with reasonable accuracy. No determinations on products high in sugar had been made, however, and it was decided to apply the method to the same samples of jelly used for the collaborative study of the malic acid methods.

TABLE 1.

Percentages of acids added to samples of jelly sent to collaborators.

SAMPLE NUMBER	MALIC ACID	CITRIC ACID	TARTARIC ACID
	per cent	*per cent*	*per cent*
1	0.35	0.38	0.00
2	0.37	0.40	0.00
3	0.37	0.29	0.17
4	0.35	0.27	0.16

TABLE 2.

Percentages of malic and citric acids found in samples of jelly sent to collaborators.

SAMPLE NO. 1. (Present: Malic acid, 0.35 per cent; citric acid, 0.38 per cent.)			SAMPLE NO. 2. (Present: Malic acid, 0.37 per cent; citric acid, 0.40 per cent.)		
ANALYST	MALIC ACID	CITRIC ACID	ANALYST	MALIC ACID	CITRIC ACID
	per cent	*per cent*		*per cent*	*per cent*
Raymond Hertwig, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, San Francisco, Cal.	0.29 0.29	0.32 0.32	F. D. Merrill, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, San Francisco, Cal.	0.29 0.29	0.33 0.33
P. L. Gowen, Bureau of Chemistry, Washington, D. C.	0.36 0.34 ----	0.30 0.29 0.32	L. Patton, U. S. Food and Drug Inspection Station, Federal Building, Buffalo, N. Y.	0.32	0.36
L. F. Hoyt, Larkin Company, Buffalo, N. Y.	---- 0.30	0.32 0.31	H. W. Haynes, U. S. Food and Drug Inspection Station, Broad Exchange Building, Boston, Mass.	0.32 0.28 0.25	0.38 0.37 ----
H. A. Lepper, Bureau of Chemistry, Washington, D. C.	0.33	0.34	H. B. Mead, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, Philadelphia, Pa.	0.29 0.26 0.31 0.27	--- 0.32 0.32 ----
M. B. Porch, H. J. Heinz Company, Pittsburgh, Pa.	---- ----	0.29 0.28	H. A. Lepper	0.35	0.36
G. W. Trainor, Armour and Company, Chicago, Ill.	0.25 0.24	0.32 0.32	T. G. Gleason, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	0.31 0.31	0.36 0.36

TABLE 2.—Concluded.

SAMPLE NO. 3. (Present: Malic acid, 0.37 per cent; citric acid, 0.29 per cent.)			SAMPLE NO. 4. (Present: Malic acid, 0.35 per cent; citric acid, 0.27 per cent.)		
ANALYST	MALIC ACID	CITRIC ACID	ANALYST	MALIC ACID	CITRIC ACID
	per cent	*per cent*		*per cent*	*per cent*
Raymond Hertwig	0.29	0.22	F. D. Merrill	0.30	0.21
	0.29	0.24		0.32	0.21
P. L. Gowen	0.26	0.23	L. Patton	0.29	0.23
	0.26	0.24			
L. F. Hoyt	0.35	0.23	H. W. Haynes	0.22	0.20
	----	0.26		0.24	0.22
				----	0.24
H. A. Lepper	0.32	0.24	H. B. Mead	0.27	0.19
				0.32	0.19
				0.26	----
				0.29	----
M. B. Porch	----	0.19	H. A. Lepper	0.31	0.24
	----	0.21			
G. W. Trainor	0.32	0.23	T. G. Gleason	0.29	----
	0.33	0.22		0.28	0.21
				0.27	0.21

Four sets of jelly samples were accordingly prepared, with the assistance of Mr. M. N. Straughn, using acid-free orange pectin made in the laboratory as a base. The finished products were colored slightly with caramel and contained between 50 and 55 per cent of total sugars and the amounts of acids shown in Table 1.

These samples were sent to the collaborators with the request that malic acid be determined in Samples 1 and 2 by Method II, and in Samples 3 and 4 by Method III, and that citric acid be determined in all samples. The results reported are collected in Table 2.

It was pointed out in last year's report that the solubility of barium citrate in alcohol will tend to lower the percentage recovery in the case of the citric acid determination. The solubility of barium malate will produce a similar effect in the case of Malic Acid Methods II and III. Furthermore, the effects of large percentages of sugar are likely to be such that a complete precipitation of the acids in jelly samples can not be expected. A series of determinations of citric acid in solutions containing amounts of sugar varying from 0.5 to 20.0 per cent were reported last year and showed a slight but undoubted decrease in percentage recovery, increasing with the percentage of sugar present. In the case of the samples containing tartaric acid also, the recovery of malic

acid will be somewhat lowered through the solution of small amounts of barium tartrate and the consequent lowering of the polariscopic reading. For these reasons Malic Acid Methods II and III were designated as approximate, and it was anticipated that the results in all the jelly samples would be somewhat low. A comparison of the actual weights of malic and citric acids found with those present, however, shows that in most cases the errors in grams of acid per 100 grams of sample are not excessive when the nature of the determinations and of the samples under examination are considered. The adoption of the methods is therefore believed to be justified.

RECOMMENDATIONS.

It is recommended—

(1) That the methods for the determination of malic acid be adopted as tentative methods with a view to later adoption as official.

(2) That the method for the determination of citric acid be adopted as a tentative method with a view to later adoption as official.

REPORT ON WINE.

By B. G. HARTMANN (Bureau of Chemistry, Food and Drug Inspection Station, Chicago, Ill.), *Associate Referee.*

The attention of the associate referee was devoted largely to a careful study of the methods for the analysis of wine.

Nothing new was submitted for collaboration. In his last report on wines, the associate referee called attention to a very satisfactory indicator for use in titrating solutions highly colored with amaranth, for acidity. This method was subjected to further study this year and a paper on the subject submitted to the association for consideration. From the satisfactory results obtained it would seem that the adoption of the method as a tentative method is warranted.

As to future work on wine, the following suggestions are made:

(1) Determination in a wine of the tartaric acid present as esters, by saponifying before determining the total tartaric acid. This seems especially desirable in fortified wines, such as sweet wines generally and sherries and ports.

(2) Determination of the acidity of a red wine by the clarification method as outlined on page 411.

(3) Determination of glycerol according to Rothenfusser's method.

TITRATION OF ACIDITY IN COLORED SOLUTIONS.

By B. G. HARTMANN (Bureau of Chemistry, Food and Drug Inspection Station, Chicago, Ill.).

The customary methods and indicators used for determining acidity in artificially colored solutions are not satisfactory. In 1914 the associate referee on wines, in the instructions to collaborators, described an indicator for use in determining acidity in solutions highly colored with amaranth.

The indicator consisted of a mixture of 50 grams of sodium sulphate and 1 gram of phenolphthalein, finely powdered. The powder was used as an outside indicator, the acid solution being spotted into the powder. The results obtained with the indicator were very satisfactory and received favorable comment from the various collaborators, and the associate referee recommended it for further study. Complying with this recommendation, the following experiments were made:

To a tartaric acid solution of known titer, weighed amounts of coal tar colors were added and the solutions titrated with N/10 alkali, using the phenolphthalein indicator, in the following manner: 20 cc. of the tartaric acid solution, containing 0.994 gram of tartaric acid per 100 cc. were transferred to a 250 cc. beaker. To this 5 cc. of the color solution containing 0.1 gram per 100 cc. were added and the mixture titrated with N/10 alkali. The indicator was placed in the cavities of a spot plate and the mixture undergoing titration spotted into the indicator until a decided pink appeared. It was found that the solution should contain about 5 cc. of alcohol to facilitate the flow of the mixture into the powder.

This scheme was tried upon the tartaric acid solution colored with the eight permitted coal tar dyes and a number of their mixtures and found to give no trouble. In all cases the end point was very sharp, there being a variation of 0.1 to 0.2 cc. of alkali for the 20 cc. portion of the mixture. It was found that the various solutions showed a titer of about 0.2 cc. of N/10 alkali in excess of the titer of the tartaric acid solution. Of the eight solutions, the one containing amaranth showed the greatest excess in this respect, amounting to 0.3 cc. of N/10 alkali over the true value.

Solutions containing methyl orange, litmus, cochineal and methyl red were also tried and gave very satisfactory results.

The organic acids, acetic, tartaric, malic, succinic, lactic and salicylic behaved very satisfactorily toward the indicator. Of the inorganic acids, phosphoric and boric were tried. Phosphoric acid may be titrated with accuracy, two hydrogen atoms being neutralized. Boric acid does not behave well, there being no distinct end point.

The indicator was tried on red wine and red grape juice. A red wine or a red grape juice is difficult to titrate because the reaction mixture passes through a series of color changes which, if not followed very closely, may leave the final end point in doubt. Generally speaking, in the titration of a red wine or grape juice, the mixture gradually acquires a brownish tint as the titration progresses and approaches neutrality, then abruptly changes to a distinct green. This is apparently the end point. If, however, a portion is tested with phenolphthalein, it will be found that the solution is still acid and several cubic centimeters of N/10 alkali are required for 20 cc. of wine to give a decided pink. Spotted into the phenolphthalein indicator, the green persists for some time, gradually changing to a muddy brown and then very suddenly to a muddy violet. This change is the end point and is rather sharp, and compares very favorably with that obtained with phenolphthalein as an inside indicator. Originally the writer had not intended the indicator for use in other solutions than those artificially colored, but it is believed that in the hands of an experienced chemist very little trouble will be encountered in titrating wines or grape juices by the method described.

No report on beer was made by the associate referee.

No report on distilled liquors was made by the associate referee.

No report on vinegar was made by the associate referee.

THE ISOLATION AND IDENTIFICATION OF GLYCEROL IN CIDER VINEGAR.

By R. W. Balcom and E. G. Grab[1] (Bureau of Chemistry, Washington, D. C.).

The determination of glycerol has in recent years become one of the most important determinations made in the analysis of vinegars for the purpose of ascertaining their purity. This determination is particularly valuable as a means of distinguishing between vinegars made by alcoholic and subsequent acetous fermentations without intermediate distillation of the alcohol, and vinegar made by the acetous fermentation of dilute distilled alcohol. Yet there does not appear to be on record anywhere in the literature any statement that the substance, glycerol, has actually been separated in a state of purity from a vinegar of known history. It seemed to us, therefore, to be worth while to isolate, and identify as such, some of the glycerol in an authentic sample of cider vinegar.

The vinegar used for this work was some that had been prepared

[1] Present address, National Fruit Product Co., Washington, D. C.

under our direct supervision from the time the apples were ground and pressed until the finished vinegar came from the generators, and was made by the alcoholic and subsequent acetous fermentations of the expressed juice of the apples.

Five separate one liter portions of this vinegar were subjected to the process for the extraction and purification of the glycerol exactly as directed in the provisional method of this association for the determination of glycerol in vinegar, except that the final treatment with silver carbonate and lead subacetate was omitted. Except in the addition of the milk of lime, a factor of 10 was used all the way through the process, since we were dealing with 1000 cc. instead of 100 cc. portions of vinegar. Likewise 200 cc. instead of 150 cc. of milk of lime were used since it was thought that the greater amount of solids in 1000 cc. of vinegar might hold back more than a proportionate amount of the acetic acid retained by the solids from 100 cc.

The five separate glycerol extracts were combined and evaporated on the steam bath, at a temperature of between 85°C. and 90°C., to a volume of about 50 cc. This solution was then divided into five approximately equal parts, each of which was subjected to distillation with sandal-wood oil under diminished pressure according to the method described by Briggs[1] for the estimation of glycerol in pharmaceutical preparations.

The aqueous solutions of glycerol obtained, after removal of the sandal-wood oil, were combined, the solution concentrated by evaporating off most of the water at low temperature, and the glycerol dried in a vacuum desiccator over sulphuric acid. Since the product was slightly yellowish in color it was dissolved in about 100 cc. of water and a small amount of previously washed eponite added to the solution. After thorough shaking the mixture was filtered, the filtrate concentrated and the glycerol dried as above described. A water-white product weighing about 10 grams was obtained. The three tests for glycerol given by Mulliken[2] were applied to this product with results identical in every way with those obtained on U. S. P. glycerol. The recrystallized benzoyl derivative of the glycerol obtained from the vinegar had a melting point of 72°C. (uncorrected) which was the same as that of the recrystallized benzoyl derivative prepared from U. S. P. glycerol, and a mixture of the two recrystallized products also melted at 72°C. (uncorrected).

As a further test, 0.3357 gram of the product was oxidized with dichromate, as in the regular method for the determination of glycerol by this method, and the results showed a purity of 98.9 per cent or practically 99 per cent.

---

[1] *J. Am. Pharm. Assoc.*, 1915, **4**: 75.
[2] Identification of Pure Organic Compounds. 1st ed., 1904, **1**: 169.

A NOTE ON THE CALCULATION OF THE VOLUME OF A LIQUID FROM WEIGHT AND SPECIFIC GRAVITY.

By R. W. Balcom (Bureau of Chemistry, Washington, D. C.).

In the method for the determination of glycerol in vinegar, which was finally adopted as a provisional method by this association in 1912, considerable emphasis is placed upon the difficulty of making accurate volumetric measurements of the strong dichromate solution used, because of the high coefficient of expansion of this strong solution, and of the changes in room temperature from day to day. To avoid this difficulty the directions state that it is advisable to determine the specific gravity and use weighed amounts of the solution. According to the directions the specific gravity is to be determined at $\frac{20°C.}{20°}$, presumably in air, since it is not customary in ordinary laboratory work to reduce weighings to vacuo. It is then stated that the weight of the solution used in a given determination, divided by the specific gravity, equals the volume used. The writer wishes to call attention to the inadequacy of these directions for calculating the volume from a given weight of solution and to point out the error which will be introduced if the calculation is made according to the directions as they now stand. This can best be done, perhaps, by giving a concrete example. A strong dichromate solution was prepared by dissolving 74.56 grams of dry, recrystallized potassium dichromate in water, adding 150 cc. of concentrated sulphuric acid, cooling, and making up to a volume of 1000 cc. at 20°C. The specific gravity of this solution was determined, using a 25 cc. pycnometer, with the following results: Weight of pycnometer filled with dichromate solution, 54.7475 grams; weight of pycnometer filled with water, 50.0095 grams; weight of pycnometer, 26.5734 grams. Hence

(1) Sp. gr., $\frac{20°C.}{20°}$, in air = 1.20217 (or 1.2022).

(2) Sp. gr., $\frac{20°C.}{4°}$, in air = 1.20005 (or 1.2001).

(3) Sp. gr., $\frac{20°C.}{4°}$, in vacuo = 1.19981 (or 1.1998).

If we take 40.0000 grams of this dichromate solution weighed in the usual way, that is, in air with brass weights, the true volume calculated by using the above values is as follows:

(1) $\frac{40.0000}{1.20217 \times 0.99718} = 33.3673$ ml.

(2) $\frac{40.0000}{1.20005 \times 0.99894} = 33.3673$ ml.

(3) $\frac{40.0344}{1.19981 \times 1.00000} = 33.3673$ ml.

or 33.37 ml. (or cc.). The calculation of the volume in each case is carried to four decimal places to show the exact agreement when the calculations are correctly made. The weight of a milliliter of water at

20°C., weighed in air with brass weights, is 0.99718 gram (or 0.9972, the value used in ordinary work). The weight of a milliliter of water at 4°C., weighed in air with brass weights, is 0.99894 (0.9989) gram. The weight in vacuo of the dichromate solution is 40.0344 grams. In these calculations, 0.99824 is taken as the density of water at 20°C., 8.4 as the density of the brass weights used, both on the basis that the density of water at 4°C. is 1.00000, and 1.20 mg. as the mean weight of 1 ml. (or cc.) of air under ordinary conditions of temperature, pressure and humidity. The volume of the dichromate solution, calculated according to the directions given in the provisional method is $\frac{40.0000}{1.20217} = 33.2732$ ml. or 33.27 ml. (or cc.), a value which is in error by 0.1 cc. or approximately 0.3 per cent, an error as great as would be caused if the strong dichromate solution were directly measured at a temperature 6° removed from 20°C., the temperature at which the solution is made up, assuming that the apparent expansion in glass of the strong dichromate solution is 0.05 per cent for each degree centigrade, as stated in the method. A similar though smaller error (about 0.1 per cent) is introduced if the weight of the strong dichromate solution, 40.0000 grams, is divided directly by the specific gravity, $\frac{20°C.}{4°}$, in air.

An error of 0.3 per cent in the determination of the small amount of glycerol present in vinegars will not appreciably affect the final result, but if the method of determining volume from weights is suggested or recommended as a means of avoiding inaccuracies in the direct measurement of the strong dichromate solution, it is obvious that the correct method of calculation should be given. If the specific gravity at $\frac{20°C.}{20°}$, in air, is used, this would be to divide the weight of the solution by the specific gravity multiplied by 0.9972. If the specific gravity, $\frac{20°C.}{4°}$, in air, is used, the factor 0.9989 should be used.

In this connection it may not be out of place to remark that in general greater attention should be given to the statement of specific gravity values. Very often the writer has seen such values expressed to four and even five decimal places, with the statement merely, that the determination was made at 20°C., or 25°C., as the case may be, which leaves it uncertain as to whether the comparison was made with water at the same or a different temperature, or whether the correction for air displacement had or had not been made. It may be argued that in most cases this makes no difference. In exact work, however, it is absolutely necessary that the conditions under which the determination is made should be fully stated and there would appear to be no good reason why this should not always be done.

R. W. Balcom (Bureau of Chemistry, Washington, D. C.), submitted a paper on "The Volatile Reducing Substance in Cider Vinegar"[1].

B. G. Hartmann and L. M. Tolman[2] (Bureau of Chemistry, Food and Drug Inspection Station, Chicago, Ill.) submitted a paper on "Vinegar Investigation—A Study of the Changes that Cider Undergoes during Fermentation and Prolonged Storage and Its Subsequent Conversion into Vinegar in Rotating Generators"[3].

REPORT ON FLAVORING EXTRACTS.

By A. E. Paul[4] (Bureau of Chemistry, Food and Drug Inspection Station, Chicago, Ill.), *Associate Referee.*

During the year, committees have been actively at work in getting the existing official, provisional and desirable unofficial methods together and into the best possible form for inclusion in the new book of methods of analysis. Under the circumstances, it did not seem desirable to attempt any new work, but it was thought preferable to submit the methods on flavoring extracts, as drawn up by the committee, to the collaborators on the subject, for criticism and suggestions. Collaborators were requested also, in case it appeared desirable, to test out experimentally any of the methods submitted on samples secured by them. It was believed that the entire chapter would thus be subjected to a most rigid and searching consideration by those chemists who are most interested in the subject, and it was hoped that suggestions would be received which might be of considerable use to the Committee on Editing Methods of Analysis as well as to the referees for the coming year.

A considerable number of very valuable responses were received from the following collaborators: A. R. Albright, Bureau of Chemistry, Washington, D. C.; E. H. Berry, U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.; C. O. Dodge, Bureau of Chemistry, Washington, D. C.; R. S. Hiltner, U. S. Food and Drug Inspection Station, Tabor Opera House Building, Denver, Colo.; Julius Hortvet, Dairy and Food Commission, Old Capitol, St. Paul, Minn.; C. D. Howard, State Board of Health, Concord, N. H.; E. R. Lyman,[5] U. S. Food and Drug Inspection Station, Arcade Annex Building, Seattle, Wash.; H. J. Wichman, U. S. Food and Drug Inspection Station, Tabor Opera House Building, Denver, Colo.

---

[1] *J. Am. Chem. Soc.*, 1917, **39**: 309.
[2] Present address, Wilson & Co., Chicago, Ill.
[3] *J. Ind. Eng. Chem.*, 1917, **7**: 759.
[4] Presented by B. G. Hartmann.
[5] Since deceased.

All of these suggestions were given very careful consideration, and with their assistance the following recommendations have been prepared.

RECOMMENDATIONS.

It is recommended—

(1) That the following changes be made in the methods as prepared by the Committee on Editing Methods of Analysis[1]:

5 First paragraph, near the beginning, change to read: "using 10 cc. the first time and 5 cc. thereafter, reserving the ethereal solution for the estimation of coumarin. To the combined ammoniacal solution add a few drops of methyl orange and acidify with hydrochloric acid. Cool and extract in a separatory funnel with 4 portions of ether, using 15 cc. each time. Evaporate the ethereal solution, etc."

5 Second paragraph, amend the first sentence to read: "and dry over sulphuric acid. The original ether extract from which the vanillin has been extracted contains the coumarin. Evaporate this ether extract at room temperature and dry over sulphuric acid".

5 Second paragraph, near middle, amend to read: "A small portion of the residue dissolved in 3 or 4 drops of hot water".

6 Change heading to "Lead Number".

6 Change the last sentence of the first paragraph as follows: "The lead number represents the amount of matter precipitated by lead acetate in 100 cc. of the extract, expressed as grams of metallic lead, and is calculated as follows:".

7 Amend to read, "employing 10 cc. of the sample".

8 Amend to read, "Evaporate 10 cc. of the extract".

14 Toward the end of the first paragraph, following "multiplied, respectively, by 4 and 8," insert a heading: "Percentage of Residual Color".

21 Omit the second paragraph: "When the extract . . . . within 0.2%".

22 Amend the first sentence as follows: "per liter to stand for 24 hours, or preferably much longer, with frequent shaking".

23 Change the first sentence to read: "Measure 10–25 cc. of extract into a 50 cc. graduated flask and make up to the mark, etc."

24 Near the middle, change "using 2 cc., etc." to read: "Using a suitable amount of the standard citral solution (2 cc. are usually satisfactory). Remove and compare the colors developed. Calculate the amount of citral present and repeat the determination, using a quantity sufficient

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 259.

to give approximately the strength of the standard. From this result calculate the amount of citral in the sample. If the comparisons are made in Nessler tubes, standards containing varying amounts should be prepared and the trial comparison made against these, the final comparison being made with standards between 1.5 and 2.5 mg., varying but 0.25 mg. For the first comparison, the following amounts will usually be found useful: 1; 1.5; 2; 2.5; 3; 3.5; and 4 mg."

37 Change to read, "Weigh 2 grams of lemon oil or 10 grams of orange oil, dilute, etc."

48 Omit the third column of the table relative to refractive indices for cassia, cinnamon and clove oils.

It is recommended—

(2) That the following be given further study:

Details for the analysis of imitation vanilla preparations containing extremely high proportions of vanillin and coumarin.

In the case of vanilla extracts, the desirability of making a preliminary qualitative test for coumarin with a view to shortening the procedure in case coumarin is absent before applying the complete official method; also possibly other methods of shortening the method of examination.

The advisability of retaining, eliminating or changing the title, "Detection of Vanilla Resins".

The applicability of Hortvet and West's method for determining alcohol in lemon and orange extracts, by calculation from the specific gravity and oil content of the sample and the approximate specific gravity of the oil; also the desirability of adopting this method officially as an alternative method, in cases of extracts composed only of the oil, alcohol and water.

A careful review of Mitchell's polarization method, for the purpose of determining the most desirable factors to be used, consideration being given to the natural variation in the oils and the disturbing influence of dilution upon the polariscopic reading of the product.

The advantage of Albright's details of the Kleber method for citral in lemon or orange oil is as follows:

After the oil has stood for 30 minutes with the phenylhydrazin and the indicator, add 1 drop of 0.5% methyl orange, run in N/2 hydrochloric acid, rotating or gently shaking all the time, until the end point appears nearly reached; then let the mixture stand a few moments until the oil separates into two layers. If a bad emulsion has formed which does not clear up in about 5 minutes, add a quantity of neutral ether sufficient to make the layers separate. Then (in the absence of ether) very gently rotate the flask, holding it close over a sheet of clear white paper, so that the upper oil layer is gradually forced, by the slight centrifugalization, out toward the walls of the flask. This results in the appearance just in the center of the surface of a small

area not covered by oil. The color of the clear solution observed perpendicularly through the mouth of the flask and this "window", and against the white background, is very easy to observe, with a little practice. Then make small additions of acid, repeating the short standing and manual centrifugalization. The end point is very distinct unless the oil treated is abnormal.

Available or new methods for determining benzoic acid in almond extract.

Howard's method[1] and the present tentative method of determining the oil in cassia, coumarin and clove extracts.

ADDRESS.

By THE HONORABLE CARL S. VROOMAN[2], *Acting Secretary of Agriculture.*

The best thing about speaking to a body of experts like this one is that it matters little what I say or do not say. Anything that I leave unsaid you can supply. Any one of you can make for himself the speech I ought to make this morning. It is true I have studied a little chemistry, but I feel a good deal like the young man who was asked whether he had ever studied German. He said yes, he had studied it for three years, but had forgotten everything he ever knew about it and had felt better ever since. About the only thing I remember about my chemistry at Harvard was the annual joke old Professor Cooke used to perpetrate on the freshman class. Holding in his hands a toy balloon and his hands shaking violently, he would say, "If this balloon were to fall from my hands we would all be hurled into eternity". As a result the freshman nearest the door usually felt an irresistible impulse to save himself by ignominious flight.

But it is not inappropriate, perhaps, that some one should say to you at this meeting a word of welcome to the city of Washington. The Department of Agriculture is not only tremendously interested in your work, but we are interested in it from various points of view. From one point of view I am competent to speak, that is from the point of view of the general public, the great body of American citizens who are not chemists, but in whose behalf the agricultural chemists of America do their work. There are one hundred million people, more or less, whose welfare is dependent to a degree upon the efficiency with which you do your work. You are developing here in this country scientific methods which most of us do not understand in their details, but from which all of us will some day derive benefits. We look to you to safeguard certain of our interests. We look to you to bear the torch of applied science a little farther forward than it has ever been taken before. We look upon

[1] *J. Ind. Eng. Chem.*, 1911, 3: 252.
[2] Present address, Wilmington, Ill.

you as constituting a sort of priesthood of knowledge, of accurate, definite, applied scientific knowledge. We do not, perhaps, think of your work except as it is brought to our attention now and then, but when we do have occasion to think of it, we do not underestimate it. Your work is one of the most important in the world, and I think that in this particular epoch in America if there is one thing that we need more than any other it is to develop accuracy and efficiency in every branch of human activity. The things for which you stand are accuracy, efficiency and scientific light thrown upon all human problems.

Now that the great war is, as we hope, drawing to a close, this country is going to play a new role in the work of the world. The war is opening to us doors that in the past have been closed. If we are able to handle our difficult problems as they arise, if we have an intelligent conception of our mission, or an intellectual preparation for our mission which will enable us to do well the things that we are going to be called upon to do, then America is destined to take her place as the material and moral leader of the world.

The Department of Agriculture is very materially interested in your work, not only as the general public is interested, but in other and more intimate ways. If there is any way in which we can cooperate with you more effectively in the future than we have in the past, we shall be delighted to do so. We are interested in you not only in a perfunctory and official way, but in a very personal way as well. Our hearts are in your work, just as I know your hearts are in your work. We have before us a great common work. Some of us who are not chemists are going to be able to cooperate with you in ways that perhaps you may not realize at the present time, and perhaps we may not realize at the present time. The future of this country depends upon the ability of the various classes, groups and interests of this country to coordinate their efforts. But one of the things that must come before a proper coordination can be effected is a more thorough understanding of other people's points of view.

The President has spoken to us about the need for a new national consciousness. Before we can develop in this country an invincible national efficiency we must develop just such a national consciousness, an ideal of nationality, a conception of the whole of which we are only a part. What is needed is more light, more information and better understanding of what other people are doing. Therefore, to you as men who are contributing to this much needed illumination of the intelligence of your people, I come, as Acting Secretary of Agriculture, to bid you welcome to Washington, and to say that the Department of Agriculture wants to help you in everything that you are undertaking for the benefit of the people of our common country.

ADDRESS BY THE HONORARY PRESIDENT.

H. W. WILEY (Good Housekeeping, Bureau of Foods, Sanitation and Health, Washington, D. C.).

It is rather a long look backward for me when I think of the beginning of this body of men and women, so long ago that it seems lost almost in the mists of the past. But it was not so long ago as my first experience in the study of chemistry, back in the early sixties, before many of you (especially the ladies) were born. That was a long time ago, and I have lived to see all of these strange transformations in chemical theories and chemical practices. In those early days, Liebig still "ruled the roost" with his ideas of chemistry, and chemistry did not amount to much then, except the study of inorganic chemistry. That was considered chemistry in those days. These ideas about physiological, pharmacological, and bacteriological chemistry had not yet arisen.

Then, later on in my career, organic chemistry was the fad. That was along in the seventies. And then everybody who studied chemistry had to be an organic chemist, and a man was not admitted to the fellowship of chemists who had not specialized in that particular direction. Then that passed away and physical chemistry arose in its place, and everybody had to be a physical chemist, whatever that means, but at any rate that is what they called it. He must have knowledge about things which we all know without ever studying chemistry.

Next came radio chemistry. That was the next fad which arose, upsetting all of our previous notions of chemistry. There was not a vestige left of what we had believed before. Madame Curie revolutionized all our views and conceptions. The term "atom" has become a misbranding under the Federal Food and Drugs Act because it means indivisible, and it was found that "atom" was not only divisible, but in point of fact might really better be called anatomy than atom because it was so cut up.

Then there has arisen a later vogue of chemistry, and that is called colloid chemistry. That is the chemistry of bodies that is described in the first chapter of Genesis as "without form and void". You can easily see who was the earliest colloid chemist. I do not need to mention His name, and yet I have never seen His name as referred to in that connection. The Lord Almighty Himself was the first colloid chemist and He had this great problem before Him: "And the earth was without form and void and darkness was upon the face of the earth".

Now I may live to see other forms, other vogues of chemistry come into popularity and understanding, and I hope that I shall, of course. Because you see I am only a young man—a bud, you might say, just beginning my life.

Some of these things that come up are pretty hard to understand sometimes, for a simple man like myself. But I read all about them and tell my wife, and she says, "I guess I know as much about that as you do", and I say, "That is true". We do not any of us understand all about them, and hence this science which we have always boasted of as being the one exact science after astronomy seems to be the most inexact science of them all. It reminds me of what I told Frank Wigglesworth Clarke about a book of his he sent me to read. He had called it "The Constants of Nature", and after I had looked it over and had met him again he asked me what I thought of his book. I replied, "I do not like the title of it". He asked, "What is wrong with the title?" I said, "You call it 'The Constants of Nature' and the constants of Nature are constantly changing". When we settle down to the very comforting view that we know something now at last that is definite and nothing can ever upset our knowledge on that particular point, something comes up to turn it upside down. That may be a comforting thought to some of us, but it is exactly the same kind of comfort you get out of the doctrine of predestination. A good Christian does not need to be comforted by the doctrine of predestination; it is only the bad man who can get any comfort out of that. He can do anything he likes and then excuse himself by saying, "Well, the Lord foreordained that I should do that before ever I was born, and so I could not help myself at all". I think I will give you a little more theology while I am about it and give you a definition of predestination, which I think is completely descriptive. You simply believe whatever is to be will be whether it ever happens or not.

Well, now, in all these variations and vagaries of chemical science, there is at least one unit that seems to have remained true to its constants all the way through—and that is the body which I am now addressing, the Association of Official Agricultural Chemists. You have not changed your purpose; you have only enlarged it. You have not failed in your devotion to this association in any respect, but, on the contrary, the devotion of the members to this association is constantly increasing.

It is true, I believe, that when we were a small body, a little family, you might say, we had better times together than we do now because we usually met in warm weather and we had at least one evening when we had something to eat and something to drink (though with my present views perhaps I ought not to allude to that form of entertainment), and we had a real family party, everybody together. And so we were a little closer than we can get now, I think. It recalls an incident I remember of a freshman who was called into Professor David Starr Jordan's office when he was President of the Indiana University. I do not recall whether he was sent for or whether he just happened in, but

anyway he came into Professor Jordan's office on some kind of bus iness. And in answer to something the president of the university sai to him, he replied: "All right, Doc, I will do that". Professor Jorda said to him, "Why so formal? Why not just call me Dave?" And i was that lack of formality we used to have in this association, a mos delightful family spirit.

Of course I know some of you by name, not very many, however Naturally, I know by your appearance that you are all members of thi association. You have a look. I feel it and I know it, but I can no describe it. There is a feeling in the air that tells me; but I do no know your names or your stations any more.

I am glad you recognized me. I suppose that was easy, though, be cause I am distinct from the others who are younger. Do you know, do not believe old men are appreciated as they should be in this country I know I did not appreciate them forty or fifty years ago as I do now Look in the banks and you will see that the men who handle money i those institutions are all young men. I suppose, though, if I looke into the penitentiaries, I should find some of the older bank cashiers. Bu in the banks themselves I see nothing but boys these days, mere young sters. Nothing but youth everywhere, when in point of fact, thoug you may not think it, the old men are the mainstays of civilizatio itself. Gray hairs are honorable and should not be despised. Even bal heads, we are told, had to be respected in Biblical times. Those wh made sport of alopecious prophets were devoured by she-bears, and I wis some such punishment might yet attend all those who fail to appreciat the worth of those who are no longer in the first blush of youth. Bu everywhere the tendency is for the old persons to get out of the way fo the young people, and I suppose that is all right. The French have saying about that—*place au jeunesse*, give way to youth. And tha seems to be practiced largely in every community and every phase o life, I think.

In the bank with which I am connected (just think, I hold an offic in a bank!), we recently passed an ordinance retiring all employees o the bank at the age of sixty. I asked them if that applied to the director also, because I did not begin to get busy until after I was sixty, and I di not want to be retired just after I had started.

But the same practice is followed in other lines of business an endeavor than banks. In the colleges and universities of learning arrangements are perfected to retire their professors at about tha age. In the Army, I believe, the age for retirement is sixty-tw and in the Navy, sixty-four. I think those are the correct ages. And i chemistry a man is usually retired, whether he wants to be or not, a about that time, and, too, without any stipend to support him in hi old age. The bank clerk is more highly appreciated than the chemistr

devotee, because over all this country of ours the banks are making arrangements to take care of their superannuated employees. The soldier is more highly appreciated for his services to mankind than is the civilian. He has an old age pension for his needs when he can no longer be in active service. Policemen are more valuable to the community than chemists. But perhaps that is no more than right—their service is so fraught with danger. You know what dangers they run into in this town every day. They may come up with a man who is robbing a house and not know it. And even school teachers are now planning for a retirement plan. Mere humanity would compel us to recognize the claim upon us of the teachers. What would this world be without the noble army of women who are devoting themselves to the profession of teaching the youth of our land? And when they get old and gray the school boards want to get rid of them, although they are surely better teachers as mature persons of tried experience than the young teachers just beginning their work. That may not count; there may be some other reasons, strange to me, why the young teachers are preferred. But at any rate, they are providing for the retirement of teachers. That is only what most of the large industries, like the Pennsylvania Railroad Company, have already done for their superannuated employees.

I am not so much averse to the distinction which is constantly being made against old age as against leaving old age to care for itself. If you calmly vote that a man past sixty is not fit for service and yet at the same time provide something for him to live on, why, that is not so bad. What I object to is for the chemist, and for every servant of that kind, after a certain age to be ruled absolutely unfit for further service and then no provision at all made for the days of his old age that are upon him. I believe this will be remedied in due time. Even now, in England, provision has been made for old age in general. Persons have been voted pensions to arrange for necessities which they are unable longer to earn—that is, persons having no income. That was done before the war and, I suppose, will be continued after the war, if it ever ceases.

But the chemist deserves some consideration. He is a public servant in the true sense of that word, and his income, as a rule, is not large. It is the chemists who invent some new process or who combine their knowledge of chemistry with a knowledge of engineering or some kindred branch who get the large salaries. Those are the chemists who are drawing handsome salaries, but the ones who do the work of the laboratory and make it possible for all kinds of business to go on, to continue to make steel and produce gunpowder and explosives of all kinds, may devote their entire lives to that service and receive but a very modest compensation.

And the men who serve in the agricultural line, the agricultural chemists of this country, perhaps for the same labor and the same expenditure of time and effort and knowledge, do more for the betterment of the world itself than any other worker. And, therefore, that sort of a chemist especially deserves the consideration of those who are promoting this retirement plan.

I want to see the veterans of this organization cared for when they have done their work. They have sacrificed their time and opportunity, and the same energy and knowledge which they gave to their problems in almost any form of business would have brought much higher financial returns than they receive as chemists, and therefore, when their work is done, or when they reach the time when the community thinks it ought to be done, ample provision ought to be made for the veterans of this service.

I do not speak for myself personally. I would not accept a pension for myself and I do not need one. I am speaking for that large army of persons who have, by reason of press of family affairs and obligations or what not, failed to accumulate any surplus, and who, when their days of active labor are over, are a charge upon their friends or the community. I have in mind now a man of that kind. He has been a faithful servant of chemistry; he has done splendid work, and he is now without employment, and is really becoming an object of charity. That does not look right to me. So now as we are getting older, because from 1884 to 1916 is a long lapse of time, we are having a lot of veterans among our members, and it seems to me the time is opportune to say a word in their behalf.

I am glad to be here this morning and perhaps I have said a few words a little off the usual line. It just happened to fall into that line of thought as it came to me how old our organization is. It brought to my mind the chemistry of old age. Old age is a chemical phenomenon. Various changes have taken place in the tissues of the body. Those are purely chemical changes, and therefore old age is a chemical problem. That has been worked out by Charles Sedgwick Minot. He studied the problem from infancy to old age and has determined the changes which took place in the protoplasm of the body. They are purely chemical changes, purely colloid chemistry, by the way. It is a colloid chemistry problem. The moment we begin to crystallize we are done for—lost. We are not able to go on living if we are not colloids. So colloid chemistry refers to us personally, and we have to take some interest in it. These chemical changes may be retarded; they can not be prevented, but they certainly can be retarded. You used to know Robert Warder, the first chemist in this country who really studied the speed of a chemical reaction. We called him "Old Speed Warder." And the speed of

a chemical reaction may be retarded, so that the secret of youth is a chemical problem. It simply means the retardation of crystallization. It means the retardation of the tissues passing into a fixed state. This is an easy problem to a certain extent, and the chemists are beginning to study this problem, too. All the fashions in chemistry are looking to this one point, so that it may be but a few years before it is solved.

The other morning my son, who is quite a theologian, by the way, said to me: "Father, God is a spirit, is He not, and He is there all the time whether we think about it or not, isn't He?" I answered, "Yes". He then asked; "God is everywhere, is He not? In the mountains, in the trees, in the stones and in the human body?" And I replied, "Sometimes he is, but sometimes his co-partner, the devil, gets into them instead". He next inquired about the age of Methuselah, and I happened to remember that he was over nine hundred and sixty-nine years, and I told him that, and it puzzled him a good deal. And then he said, "How old was Adam?" But I was not so sure of that, and I did not have the records before me, but I told him Adam was over six hundred at least, and he asked, "And the lady, how old was she?" My answer was, "Ladies never tell their ages, so I can not give you the information you desire".

But if we perfect this chemistry of retardation and if it is taught and practiced, then the women will no longer be ashamed to say they are forty, because they will still have the bloom of youth. And that is one of the problems the chemists of this age will be studying. How can humanity be so protected against the ravages of the body as to harden the tissues; how can this retardation be made practical? And there is no doubt in my mind but that it can and will be, and that the human span of life will be greatly lengthened and youth extended; and then we shall not need to retire at sixty, perhaps not at seventy, maybe not at eighty, because youth will be projected much further into the future than it is at the present time. These are some of the problems in colloid chemistry which are to be solved in the future, my friends.

I again say to you that it has been a great pleasure to me to be privileged to be here and to look into your faces, many of them so strange to me, but all dear to me because of the industry in which you are engaged for the betterment of humanity.

The meeting adjourned at 12.30 p. m. to reconvene at 1.30 p. m.

ERRATA.

Page 193, Test, second paragraph, line 2.—Omit formula.

Page 262, line 9.—Change the second formula to read:

"$\frac{8}{G+40+\frac{3\,S^2}{1000\,G^2}}$".

SECOND DAY.

TUESDAY—AFTERNOON SESSION.

REPORT ON SPICES.

By H. E. SINDALL[1] (Weikel & Smith Spice Co., Philadelphia, Pa.), *Associate Referee.*

The work has been limited to a continuation of the study of the associate referee's modification of the distillation method for water in whole spices. Samples of Zanzibar cloves, Jamaica allspice and Lampong pepper were sent to fifteen collaborators with a copy of the method, and a photograph of the apparatus as used by the associate referee. Comments and recommendations were requested.

Moisture in spices.

ANALYST	ZANZIBAR CLOVES	JAMAICA ALLSPICE	LAMPONG PEPPER
	per cent	*per cent*	*per cent*
Sylvana Elliott, Food and Drug Department, Vermilion, S. Dak.	----	6.20	----
	----	6.10	6.50
	----	6.58	6.80
T. G. Gleason, U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.	12.4	7.40	9.40
	12.2	7.80	10.40[a]
	13.2[b]	7.50	13.00[c]
J. H. Bornmann, U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.	7.90	5.44	6.60
	8.00	5.20	7.40
W. C. Geagley, Food and Drug Department, Lansing, Mich.	11.60	7.20	8.80
	12.20	7.20	8.60
M. B. Porch, H. J. Heinz Company, Pittsburgh, Pa.	----	7.00	7.20
	----	7.00	7.20
R. J. Quinn, Morris and Company, Union Stock Yards, Chicago, Ill.	12.90	7.65	9.90
	12.90	7.65	9.90
C. H. LaWall, 39 South Tenth Street, Philadelphia, Pa.	14.00	8.50	10.50
W. B. Smith, Bureau of Animal Industry, Kansas City, Kans.	13.70[d]	8.50	9.20
	13.10	8.60	9.60
C. L. Black, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, Philadelphia, Pa.	13.30	8.30	10.70
	13.90	8.20	10.40
G. N. Watson, University of Kansas, Lawrence, Kans.	11.00	9.00	9.85
	10.80	9.10	10.00

[a] Followed directions without drying connections.
[b] Heated 45 minutes 170–180°C.
[c] Continued distillation for 1 hour.
[d] Distilled 45 minutes.

[1] Present address, Austin, Nichols & Co., Brooklyn, N. Y.

The method sent out follows:

Place 50 grams of whole spice in a distillation flask with 150 cc. of kerosene, whirl the flask several times to bring the oil into contact with each particle of spice. Place the flask on an asbestos board cut so that the bottom of the flask extends below the surface. Place a wire gauze with an asbestos center about ½ inch below the bottom of the flask. The object is to keep the flame out of direct contact with the flask. The asbestos board serves to keep the heat uniform. Connect the flask directly with a vertical condenser. Insert a thermometer through the stopper of the distillation flask extending into the oil. Adjust the flame so that about 20 minutes will be required to reach the temperature of 170°C. and collect the distillate in a graduated cylinder or burette. Extinguish the flame, after which the thermometer will show a slight gradual increase in temperature. As soon as the water stops dropping from the condenser tube, which usually requires from 4–6 minutes, the operation is complete. Multiply the volume of the water layer by 2 to obtain the percentage of moisture.

DISCUSSION.

The difference in the results reported by the different analysts may be in part explained by the difference in the apparatus used, and the lack of experience with the method. Consideration should also be given to the fact that all the samples were not examined by the analysts for some time after receipt. It is possible therefore that some moisture was lost previous to analysis. It seems that the method warrants further study, particularly as to size and dimensions of the apparatus and the length of time of heating.

The associate referee's attention was called to the necessity of having a definite method of sampling spices and preparation for analysis. This is a most important proposition, since some spices have a tendency to separate after being ground.

RECOMMENDATIONS.

It is recommended—

(1) That the associate referee's modification of the distillation method for water in whole spices be given further study with particular reference to the size and dimensions of the apparatus and length of time of heating.

(2) That the subject of sampling and grinding and the preparation for analysis of each spice be studied.

REPORT ON BAKING POWDER.

By H. E. Patten (Bureau of Chemistry, Washington, D. C.),
Associate Referee.

Following the recommendations of the referee for 1915, a further study of the value of the Exner and Wichmann methods for lead determination in baking powders has been conducted. Last year these methods were studied for their value in determining lead quantitatively from comparatively simple solutions. This year the study has been continued, using synthetic samples of phosphate baking powders where, in addition to the quantitative determination of the lead itself, the further difficulties of separating the lead from the complex mixture of ingredients have been encountered.

DESCRIPTION OF SAMPLES.

The samples sent out consisted of a synthetic baking powder mixed from ingredients in which the lead content had been previously determined. Each sample weighed 100 grams and consisted of 56 grams of monocalcium phosphate, 25.5 grams of sodium bicarbonate and 18.5 grams of starch. The ingredients were carefully mixed, and the collaborators instructed to use the entire contents of an individual sample can for each determination. The lead content of the baking powder, calculated from the determinations on the individual ingredients as made by Mr. Seeker and Mr. Chittick, was 7 parts per million, or 0.0007 gram of lead in each 100 gram sample.

DESCRIPTION OF METHODS.

The methods used in the collaboration were the Exner method (modified for a 100 gram sample) and the Wichmann method[1]. Method II was used as published. Method III was modified, using a 100 gram sample and one-half the quantity of all reagents.

REPORTS OF COLLABORATORS.

Reports were received from five collaborators. A summary of the results of the lead determinations is given in Table 1, as parts per million and as actual weight of lead in mg. per 100 grams of sample.

From an examination of Table 1, it will be seen that the results vary greatly, not only as a whole, but in duplicate samples examined by the same analyst. The variations between determinations are as pronounced in one method as in the other. The results with the Exner method run about twice as high as those with the Wichmann method and about twice the actual lead content. The average of the results with the

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 348.

Wichmann method agrees fairly well with the actual content of lead in the sample, but due to the wide variations in individual results the average can not be considered of much import.

TABLE 1.

Lead in phosphate baking powder Sample No. 161, as reported by analysts[a].

ANALYST	EXNER METHOD		WICHMANN METHOD	
	Mg. of lead per 100 grams	Parts per million	Mg. of lead per 100 grams	Parts per million
J. O. Clarke, Department of Agriculture, Atlanta, Ga.	2.0	20	1.4	14
	3.1	31	0.8	8
	---	--	0.6	6
	---	--	0.4	4
	---	--	0.3	3
L. F. Hoyt, Larkin Company, Buffalo, N. Y.	0.0	0	0.0	0
	0.0	0	0.0	0
J. R. Davies, Calumet Baking Powder Co., Chicago, Ill.	1.2	12	0.5	5
	1.4	14	1.0	10
A. L. Burns, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	1.8	18	0.4	4
	1.0	10	1.2	12
E. R. Lyman[b], U. S. Food and Drug Inspection Station, Arcade Annex Building, Seattle, Wash.	0.0	0	0.0	0
	0.0	0	0.0	0

[a] Lead content of sample No. 161 as determined from analysis of separate ingredients was 0.7 mg. lead per 100 grams or 7 parts per million.
Each 100 grams of sample contained 56 grams of calcium monophosphate, 25.5 grams of sodium bicarbonate, 18.5 grams of cornstarch.
[b] Since deceased.

The collaborators were also asked to report on the time consumed in operations and the amount of wash water used in the various steps. The time consumed varied greatly with the different analysts, and of course depended upon the amount of other work carried on at the same time. However, a comparison of the relative time consumed for the Exner and for the Wichmann method for each analyst shows that in every case the time necessary with the Exner method was from two to three times that required by the Wichmann method.

The reports on the volume of water used in washing precipitates showed excessively large quantities needed with the Exner method. The average amount of water in this method was 8 or 9 liters, most of which was used with the sulphid precipitates. Since the solubility of lead sulphid is 0.15 mg. per liter of solution saturated with hydrogen sulphid[1], it can readily be seen that there is bound to be a loss of lead

[1] George von Hevesy and Friz Paneth. *Z. anorg. Chem.*, 1913, **82**: 323.

which will be a large proportion of the total lead present, especially where such small quantities as 20 parts per million are involved.

DISCUSSION OF THE METHODS AND DIFFICULTIES ENCOUNTERED IN THEIR USE.

Exner method.—The collaborators found the Exner method to be very tedious and laborious. The precipitates were bulky and the quantities of wash water needed exceedingly large, thus giving opportunities for loss of lead. The iron present in the baking powder interfered greatly with the determination, contributing to the bulkiness of precipitates, and undoubtedly holding back part of the lead. In some cases the amount of lead found was low, due to being held from solution by the iron; in others the high lead results were due probably to the presence of iron salts with the lead chromate weighed.

The opinion of every collaborator is that, because of the excess of time, labor and materials required, the Exner method is impracticable. Last year this method was tentatively recommended because it showed its reliability in determining lead quantitatively in fairly simple solutions. The results of the work this year show that, when the complications due to the complex mixture of ingredients in baking powder are involved, the method is not accurate. With these considerations it would seem useless to carry on further work with the Exner method. It is recommended that the Exner method be dropped from the methods of the association and no further study be made of it.

Wichmann method.—In the work with this method, bulky sulphid precipitates were also encountered. The bulkiness is caused largely by a precipitation of phosphates when the solution is made slightly alkaline, as called for by the directions given in the method. Several of the collaborators suggest that the sulphid precipitation be carried out with the solution slightly acid, in order to avoid this difficulty. The large amount of iron present gave difficulty, and led to inaccurate results. Mr. Chittick and Mr. Seeker both suggest treatment of the combined iron and lead sulphates with dilute sulphuric acid, and the separation of the lead sulphate by the addition of alcohol. While this procedure would probably eliminate the iron, it adds to the time required, which is a disadvantage. The general opinion of the collaborators is that this method is a fairly quick one, and that with a few changes it has possibilities of becoming an accurate and valuable method. The referee recommends that a further study of the Wichmann method and modifications for its improvement be made.

NEW METHODS.

The deposition of the lead in baking powder by electrolysis offers a means of shortening the determination. Dr. T. J. Bryan (Calumet Baking Powder Company, Chicago, Ill.) has submitted a modification of the Corper method for electrolytic determination of lead, which he has found very satisfactory when applied to phosphate baking powders. It is recommended that this method be studied during the coming year.

ACKNOWLEDGMENT.

The associate referee wishes to thank the collaborators and analysts for their interest and for the time generously given to this collaboration, and Messrs. A. F. Seeker[1] (U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.), J. R. Chittick (Jaques Manufacturing Company, Chicago, Ill.) and H. A. Lepper (Bureau of Chemistry, Washington, D. C.) for their assistance in determining the lead content of the separate ingredients from which the collaborative samples were made up, and especially Mr. G. H. Mains (Physical Chemical Laboratory, Bureau of Chemistry, Washington, D. C.) for assistance on the referee's report.

RECOMMENDATIONS.

It is recommended—

(1) That the Exner method for the gravimetric determination of lead (now a tentative method) be dropped from the association methods, and that no further study of it be made.

(2) That a further study be made of the Wichmann method and modifications for its improvement.

(3) That a study be made of Bryan's modification of the Corper method for the electrolytic determination of lead in baking powders.

No report on meat and fish was made by the associate referee.

REPORT ON FATS AND OILS.

By R. H. KERR (Bureau of Animal Industry, Washington, D. C.), *Associate Referee.*

Two methods were studied: (1) A modification of the present provisional method for detection of the adulteration of lard with solid fats based on the work of Bömer[2]; and (2) a modification of the potassium salt-acetone method for the separation of solid and liquid fatty acids[3].

[1] Since deceased.
[2] *Z. Nahr. Genussm.*, 1913, **25**: 367; **26**: 559.
[3] S. Fachinini and U. Dorta. *Chem. Rev. Fett. Hanz. Ind.*, 1914, **19**: 77.

The list of would-be collaborators was divided and samples for one method sent to one list and those for the other method to another.

MODIFIED METHOD FOR DETECTION OF ADULTERATION OF LARD WITH SOLID FATS.

This method represents an attempt to modify the present provisional method, taking into consideration Bömer's discovery of the specific glyceride in lard which is responsible for the difference in melting points of the crystallized glycerides of lard and tallow. Bömer, it will be remembered, discovered that lard does not contain tristearin, but that its principal saturated glyceride is α-palmito-distearin, while beef and mutton tallow have as their principal saturated glycerides β-palmito-distearin, and tristearin. This difference in the character of the saturated glycerides is the fundamental fact which lies at the bottom of all the methods ever devised for detecting the adulteration of lard with solid fats. In the light of his new knowledge, Bömer devised a method for detecting tallow in lard which, while based on sound principles and accurate chemical knowledge, was yet cumbersome and inefficient.

The character of the method was such, however, that by a slight and simple modification it could be made to serve as an admirable check on the Emery method. The modified method sent out to the collaborators for study was as follows:

Weigh out 5 grams of the filtered fat into a glass-stoppered cylinder graduated to 25 cc., add warm acetone until the 25 cc. mark is reached. Shake the cylinder until the contents are thoroughly mixed, and then let stand in a suitable place at 30°C. After 18 hours remove the cylinder and carefully decant the supernatant acetone solution from the crystallized glycerides, which are usually found in a firm mass at the bottom of the cylinder. Add warm acetone in three portions of 5 cc. each from a small wash bottle, care being taken not to break up the deposit while washing and decanting the first two portions. Actively agitate the third portion in the cylinder, and by a quick movement transfer it with the crystals to a small filter paper. Then wash the crystals with five successive small portions of the warm acetone with the use of the wash bottle and remove the excess acetone from them by suction. Transfer the paper with its contents to a suitable place, spread it out, and break up any large lumps of the glycerides by gentle pressure. When dry thoroughly comminute the mass and determine the melting point of the crystals.

After the melting point of the crystallized glycerides has been determined, transfer them to a 50 cc. beaker, add 25 cc. of approximately N/2 alcoholic potassium hydroxid and heat on the steam bath until saponification is complete. Pour the solution into a separatory funnel containing 200 cc. of water, acidify, add 50 cc. of ether and shake. Draw off the acid layer and wash at least three times with water. Transfer the ether solution to a clean, dry 50 cc. beaker, drive off the ether on the steam bath and finally dry the acids at 100°C. Allow the acids to stand for at least 2 hours. Dry and determine the melting point in the same manner as described for crystals. If the melting point of the glycerides plus twice the difference between the melting point of the glycerides and the melting point of the fatty acids is less than 71°C., regard the lard as adulterated.

The composition of the five samples sent out for collaborative work was as follows:

Sample 1—Lard + 3 per cent oleo stearin.
Sample 2—Lard + 3 per cent hydrogenated cottonseed oil.
Sample 3—Pure lard.
Sample 4—Lard + 5 per cent hydrogenated whale oil.
Sample 5—Lard + 10 per cent beef tallow.

Cooperative work on the determination of melting point, etc.

ANALYST AND SAMPLE NUMBER	GLYCERIDES (A)	ACIDS (B)	A+2 (A −B)	REMARKS
W. B. Smith, Bureau of Animal Industry, Kansas City, Kans.	°C.	°C.	°C.	
Sample 1	61.4	57.2	69.8	Adulterated
Sample 2	61.2	60.7	62.2	Adulterated
Sample 3	63.6	57.3	76.2	Pure
Sample 4	60.6	56.6	68.6	Adulterated
Sample 5	61.7	58.2	68.7	Adulterated
C. T. Allcutt, Bureau of Animal Industry, Kansas City, Kans.				
Sample 1	61.5–61.6	58.4 –58.0	67.7–68.8	Adulterated
Sample 2	61.0–61.2	60.5 –60.7	62.0–62.6	Adulterated
Sample 3	63.4–63.6	57.2 –57.4	75.8–76.0	Pure
Sample 4	59.5–59.8	56.75–56.7	65.0–66.0	Adulterated
Sample 5	61.6–61.6	58.6 –58.2	67.6–68.4	Adulterated
L. B. Burnett, Bureau of Chemistry, Washington, D. C.				
Sample 1	61.2	58.0	67.6	Adulterated
Sample 2	60.7	60.2	61.7	Adulterated
Sample 3	62.8	56.4	75.6	Pure
Sample 4	59.8	57.2	65.2	Adulterated
Sample 5	61.4	59.0	66.2	Adulterated
T. R. LeCompte, Bureau of Animal Industry, Washington, D. C.				
Sample 1	62.2	58.8	69.0	Adulterated
Sample 2	62.0	61.3	63.4	Adulterated
Sample 3	64.0	58.6	74.8	Pure
Sample 4	61.0	57.8	67.4	Adulterated
Sample 5	62.3	58.4	70.1	Adulterated
R. H. Kerr, Bureau of Animal Industry, Washington, D. C.				
Sample 1	61.8	58.6	68.2	Adulterated
Sample 2	61.6	61.2	62.4	Adulterated
Sample 3	64.0	58.4	75.2	Pure
Sample 4	60.8	57.6	67.2	Adulterated
Sample 5	62.2	58.2	70.2	Adulterated

All five samples were correctly reported by all collaborators.

POTASSIUM SALT-ACETONE METHOD FOR THE SEPARATION OF SOLID AND LIQUID FATTY ACIDS.

In this work it was found necessary to change the method slightly after it had been sent out. In the revised form the method is as follows:

Saponify a sufficient quantity of the oil or fat to set free the fatty acids. The process of saponification and preparation of the fatty acids used for the titer test may be employed. Take particular care to avoid overheating or scorching the soap or fatty acids.

Next determine the iodin number of the mixed fatty acids. Dissolve 5 grams of the fatty acids in 150 cc. of pure, warm acetone, add slowly, drop by drop, a sufficient amount of N/2 potassium hydroxid solution to precipitate the estimated amount of saturated fatty acids present, and a small amount in excess. Calculate the amount of potassium hydrate required from the iodin number and the known or supposed iodin number of the liquid fatty acids of the fat or oil under examination. Allow the mixture to cool to room temperature, place in ice-water and finally leave the flask in ice-water overnight, or for at least 3 hours. Filter off the solution from the precipitated potassium salts and wash the latter twice by decantation and twice on the filter with cold acetone. Wash the precipitate, with hot water, into the flask in which precipitation took place, add sufficient dilute sulphuric acid to decompose the salts, heat until the separated acids form a clear layer on top of the acid solution, cool, pour off the acid solution, add water, heat until the acids melt and form a clear layer, again cool, wash, transfer to a tared beaker, dry, and weigh.

Pour the acetone filtrate and washings into a large separatory funnel, add 500 cc. of water and sufficient dilute sulphuric acid to break up all potassium salts, add 200–300 cc. of ether, shake, draw off the acid layer, wash the ether layer three times with water, evaporate the ether and dry under vacuum or in a current of carbon dioxid or hydrogen and finally determine the iodin number of the liquid acids.

A sample of cottonseed oil and a sample of inedible tallow were sent to each collaborator. Collaborators were requested to determine the percentage of solid acids and iodin number of the liquid acids on each sample and if possible to compare the results obtained with those obtained by the present provisional method. The following results were reported:

Cooperative work on liquid and solid acids.

ANALYST	SOLID ACIDS		IODIN NUMBER OF LIQUID ACIDS	
	Tallow	Cottonseed oil	Tallow	Cottonseed oil
	per cent	*per cent*		
A. G. Woodman, Massachusetts Institute of Technology, Boston, Mass.	58.8 60.6	31.9 31.5	90.0 88.7	147.7 140.3
L. B. Burnett	38.34	17.24	66.24	80.00
L. B. Burnett[a]	45.27 45.78 44.82	24.19 23.96	92.00	143.30
R. H. Kerr	48.07	23.58	83.37	141.50

[a] By tentative lead-salt-ether method.

While these results may be regarded as promising and while experience with the method appears to justify further study, it is clearly evident that the method as presented here is not capable of taking the place of the present tentative lead-salt-ether method. It is regarded as worthy of further study.

RECOMMENDATIONS.

It is recommended—

(1) That the present provisional method for the detection of beef fat in lard be changed to permit the preparation of the glycerides by crystallization from acetone at 30°C. or from ether at 18 to 20°C. at the option of the analyst, instead of only from ether at 18 to 20°C. as at present, and that the second paragraph of the method studied, that dealing with the preparation and determination of the melting point of the fatty acids, be made a part of the method.

(2) That the potassium-salt-acetone method for the separation of liquid and solid fatty acids be given further study.

REPORT ON DAIRY PRODUCTS.

By JULIUS HORTVET (State Dairy and Food Commission, St. Paul, Minn.), *Associate Referee.*

The work of the past two years has included—

(1) A further study of the Roese-Gottlieb method as applied to ice cream, milk powders, and malted milk.

(2) A further study of modifications of the Babcock centrifugal method as applied to evaporated milk.

A description of the following methods was forwarded to the collaborators—

(1) The Roese-Gottlieb method for evaporated milk and condensed milk.

(2) The Manchester modified Babcock test.

(3) The Hunziker modified Babcock test.

MANCHESTER METHOD.

Weigh 9 grams of the sample into an 8 or 10 per cent milk test bottle and set the bottle into a bath of ice-water until thoroughly chilled. Add 7.5 cc. of sulphuric acid (sp. gr. 1.84). The acid should be poured as rapidly as practicable into the milk bottle, which is inclined to one side in order that the acid may settle to the bottom of the sample with as little admixture as possible. The contents of the tube are then immediately mixed and the shaking continued until the mixture is homogeneous.

Allow the test bottle to stand at room temperature for 15 minutes and fill nearly to the base of the neck with hot water, thoroughly mix and submerge in a boiling water bath for 15 minutes, then centrifugalize for 7 minutes at about 1200 revolutions per minute. Add hot water to make the fat column rise into the scale portion of the neck, and centrifugalize an additional 2 minutes. Read the fat column "a" from the extreme bottom to the extreme top, and "b" from the extreme bottom to the lower line of the upper meniscus. Multiply the reading "b" by 2 and add 0.15 to the result to obtain the per cent of fat in the sample. Also obtain the per cent of fat by adding readings "a" and "b".

NOTE.—Better results are obtained if the sulphuric acid employed is also cold when first added. If the weather be warm the acid bottle should be kept in a refrigerator, or a small supply may be chilled in a bottle by submerging in ice-water.

HUNZIKER METHOD.

Weigh 4.5 grams of the well-mixed sample into an 8 or 10 per cent milk test bottle, add 17.5 cc. of water, then add 17.5 cc. of sulphuric acid (sp. gr. 1.84), and shake until the curd in the test bottle is completely dissolved. Centrifugalize at a speed of about 1200 revolutions per minute for 5 minutes. Mix equal portions of water and sulphuric acid in a glass beaker, fill the test bottle to the zero mark with hot diluted acid and centrifugalize an additional 2 minutes, then add hot water to make the fat column rise into the scale portion of the tube and centrifugalize 1 minute. Read the fat column from the extreme bottom to the extreme top, and multiply the reading by 4.

The following samples were sent to the collaborators: (1) Plain ice cream; (2) evaporated milk; (3) sweetened condensed milk; (4) dried milk; (5) malted milk.

TABLE

Results by Roese-

ANALYST	ICE CREAM		SWEETENED CONDENSED MILK	
	Official method	Mojonnier apparatus	Official method	Mojonnier apparatus
	per cent	*per cent*	*per cent*	*per cent*
W. L. Adams, State Board of Health, Concord, N. H.	7.37 7.49 7.37	---- ---- ----	---- ---- ----	---- ---- ----
V. B. Bonney, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, San Francisco, Cal.	Had separated		9.46 9.57	---- ----
E. M. Bailey, Agricultural Experiment Station, New Haven, Conn.	Badly churned		---- ---- ----	---- ---- ----
F. E. Schunk, Wisconsin Condensed Milk Co., Burlington, Wis.	---- ----	---- ----	9.672 9.680	9.658 9.664
R. Hertwig, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, San Francisco, Cal.	Fat separated in lumps		---- ----	---- ----
Carnation Milk Products Co., Oconomowoc, Wis.	----	----	----	----
D. G. Morgan, Agricultural Experiment Station, Stillwater, Okla.	7.58 7.68	---- ----	9.35 9.35	---- ----
J. F. Snell, Macdonald College, Quebec, Canada.	7.74 7.83	---- ----	9.66 9.54	---- ----
E. H. Berry, U. S. Food and Drug Inspection Station, 1625 Transportation Building, Chicago, Ill.	7.68 7.61 ----	---- ---- ----	9.40 9.45 9.50	---- ---- ----
C. C. Forward, Inland Revenue Department, Halifax, N. S.	7.70 7.76 7.72 7.71	---- ---- ---- ----	---- ---- ---- ----	---- ---- ---- ----
Mojonnier Bros. Co., Chicago, Ill.	---- ----	---- ----	---- ----	9.687 9.683
David Klein, Illinois Division of Foods and Dairies, Chicago, Ill.	7.80 7.82	---- ----	9.77 9.77	---- ----
M. L. Jones, Sears, Roebuck & Co., Chicago, Ill.	7.07[a] 7.07[a] 7.02[a]	Condition unsatisfactory	9.64 9.64 9.62	---- ---- ----
C. N. Austin, Sears, Roebuck & Co., Chicago, Ill.	6.87[a] 6.87[a] 6.82[a]	Condition unsatisfactory	9.62 9.59 9.56	---- ---- ----

[a] Not included in maximum and minimum results.

1.

Gottlieb method.

EVAPORATED MILK		DRIED MILK			MALTED MILK		
Official method	Mojonnier apparatus	Alkaline extraction	Acid extraction	Mojonnier apparatus	Alkaline extraction	Acid extraction	Mojonnier apparatus
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
7.78	----	1.39	1.43	----	7.38	7.72	----
7.85	----	----	----	----	----	----	----
7.98	----	----	----	----	----	----	----
7.67[a]	----	1.14	1.3	----	6.98	7.84	----
7.64[a]	----	1.13	1.34	----	6.92	7.76	----
7.90	----	1.45	1.39	----	7.52	7.70	----
7.95	----	1.32	1.48	----	7.50	7.60	----
----	----	1.40	1.49	----	7.58	7.70	----
7.876	7.888	1.083	1.362	1.098	7.23	----	7.38
7.878	7.892	1.088	----	1.084	7.33	----	7.46
7.94	----	1.28	1.50	----	7.88	7.26	----
7.97	----	1.23	1.47	----	7.82	7.30	----
7.86	7.86	1.31	----	1.31	7.04	----	7.04
7.93	----	1.45	1.36	----	6.72	7.26	----
7.90	----	1.47	1.29	----	6.80	7.14	----
7.93	----	1.15	0.90	----	7.26	6.70	----
7.97	----	1.10	0.99	----	6.80	6.62	----
7.95	----	1.00	----	----	7.12	----	----
7.99	----	1.30	1.25	----	7.60	7.50	---
7.85	----	1.40	1.25	----	7.70	7.50	----
----	----	----	----	----	7.65	----	----
7.95	----	1.17	1.40	----	7.26	8.10	----
7.98	----	1.35	1.40	----	7.26	8.20	----
7.99	----	1.23	1.38	----	7.50	8.14	----
7.97	----	1.22	1.50	----	7.26	8.20	----
----	7.888	1.20	----	----	7.50	----	----
----	7.891	----	----	----	7.50	----	----
7.96	----	1.29	----	----	7.70	----	----
7.96	----	1.31	----	----	7.70	----	----
7.83	----	1.09	1.24	----	7.16	7.18	----
7.86	----	1.13	1.30	----	7.12	7.22	----
----	----	----	1.27	----	7.18	7.34	----
7.90	----	1.12	1.27	----	7.16	7.30	----
7.88	----	1.09	1.25	----	7.16	7.30	----
7.88	----	----	1.24	----	7.14	7.26	----

TABLE

ANALYST	ICE CREAM		SWEETENED CONDENSED MILK	
	Official method	Mojonnier apparatus	Official method	Mojonnier apparatus
	per cent	*per cent*	*per cent*	*per cent*
J. T. Keister, Bureau of Chemistry, Washington, D. C.	7.77	----	9.675	----
	7.82	----	9.691	----
	----	----	9.744	----
L. W. Ferris, Bureau of Chemistry, Washington, D. C.	----	----	9.73	----
	----	----	9.71	----
	----	----	----	----
W. D. Strack, Borden's Condensed Milk Co., New York, N. Y.	7.69	7.69	9.74	9.72
	7.68	7.69	9.72	9.72
	----	----	9.73	----
	----	----	----	----
	----	----	----	----
H. Hoffmann, State Dairy and Food Commission, St. Paul, Minn.	7.65	7.64	9.75	9.62
	7.68	----	9.72	9.64
	7.65	----	9.73	----
P. J. Donk, National Canners Association, Washington, D. C.	8.10	----	9.88	----
	8.15	----	9.87	----
	8.09	----	9.88	----
Maximum	8.15	----	9.88	----
Minimum	7.37	----	9.35	----

TABLE 2.

Results on evaporated milk by modified Babcock methods.

ANALYST	MANCHESTER				HUNZIKER		OFFICIAL METHOD (RESULTS AVERAGED FROM TABLE 1)
	Readings		Fat		Reading	Fat	Fat averages
	a	b	a+b	b×2+0.15	a	a×4	
			per cent	*per cent*		*per cent*	*per cent*
W. L. Adams	----	----	9.50[a]	9.37[a]	----	8.20[a]	----
	----	----	9.50[a]	9.37[a]	----	9.00[a]	----
	----	----	10.00[a]	9.89[a]	----	9.00[a]	7.87
	----	----	----	----	----	9.00[a]	----
V. B. Bonney	3.80	3.60	7.40	7.35	1.90	7.60	----
	3.80	3.60	7.40	7.35	1.90	7.60	7.655
E. M. Bailey	4.09	3.80	7.89	7.75	2.00	8.00	----
	----	----	----	----	2.00	8.00	7.93

[a] Directions for method not followed; results unsatisfactory.

1.—Concluded.

EVAPORATED MILK		DRIED MILK			MALTED MILK		
Official method	Mojonnier apparatus	Alkaline extraction	Acid extraction	Mojonnier apparatus	Alkaline extraction	Acid extraction	Mojonnier apparatus
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
7.963	----	1.225	1.43	----	7.14	7.44	----
7.986	----	1.23	1.434	----	7.27	7.509	----
----	----	1.19	----	----	----	----	----
7.91	----	1.31	1.37	----	7.65	7.97	----
7.94	----	1.24	1.48	----	7.79	7.69	----
----	----	----	1.34	----	7.52	7.48	----
7.92	7.91	1.30	1.40	----	7.35	7.26	----
7.91	7.92	1.25	1.43	----	7.38	7.23	----
----	7.91	1.25	1.49	----	7.35	7.23	----
----	----	1.28	----	----	7.31	7.22	----
----	----	1.40	----	----	----	----	----
7.91	7.90	1.34	1.36	----	----	----	----
7.95	7.89	----	1.33	----	----	----	----
7.95	----	----	----	----	----	----	----
7.89	----	1.44	----	----	7.46	----	----
7.89	----	1.41	----	----	7.43	----	----
7.90	----	1.49	----	----	7.45	----	----
7.99	----	----	----	----	----	----	----
7.78	----	----	----	----	----	----	----

TABLE 2.—Continued.

ANALYST	MANCHESTER				HUNZIKER		OFFICIAL METHOD (RESULTS AVERAGED FROM TABLE 1)
	Readings		Fat		Reading	Fat	Fat averages
	a	b	a+b	b×2+0.15	a	a×4	
			per cent	*per cent*		*per cent*	*per cent*
F. E. Schunk	3.96[b]	3.76[b]	7.72	7.67	1.957[b]	7.83	7.877
R. Hertwig	----	----	8.01	8.01	----	7.74	----
	----	----	8.04	8.00	----	7.90	7.95
	----	----	7.91	7.82	----	7.96	----
	----	----	8.15	8.11	----	7.86	----
Carnation Milk Products Co.	----	----	8.00	----	----	----	7.86
D. G. Morgan	----	----	8.50	8.50	----	----	7.915
J. F. Snell	4.04	3.85	7.89	7.85	unsatisf	actory	7.95
E. H. Berry	4.00	3.80	7.80	7.75	1.91	7.64	7.92

[b] Average of several determinations.

TABLE 2.—Concluded.

ANALYST	MANCHESTER				HUNZIKER		OFFICIAL METHOD (RESULTS AVERAGED FROM TABLE 1)
	Readings		Fat		Reading	Fat	Fat averages
	a	b	a+b	b×2+0.15	a	a×4	
			per cent	*per cent*		*per cent*	*per cent*
C. C. Forward	4.00	3.74	7.74	7.63	2.00	8.00	----
	4.03	3.80	7.83	7.75	1.94	7.76	----
	4.01	3.78	7.79	7.71	1.92	7.68	----
	4.00	3.74	7.74	7.63	1.92	7.68	----
	4.02	3.80	7.82	7.75	2.00	8.00	----
	4.02	3.80	7.82	7.75	1.94	7.76	7.97
David Klein	4.00	3.80	7.80	7.75	1.90	7.60	7.96
M. L. Jones	4.00	3.85	7.85	7.85	----	----	----
	4.00	3.85	7.85	7.85	----	----	7.85
C. N. Austin	4.03	3.88	7.91	7.91	----	----	----
	4.04	3.90	7.94	7.95	----	----	7.89
J. T. Keister	----	----	7.88	7.83	----	7.98	----
	----	----	7.86	7.81	----	7.98	7.974
L. W. Ferris	4.00	3.80	7.80	7.75	1.97	7.88	----
	4.00	3.81	7.81	7.77	1.99	7.96	7.93
W. D. Strack	----	----	----	----	1.90	7.60	----
	----	----	----	----	1.95	7.80	7.91
H. Hoffmann	4.00	3.80	7.80	7.75	1.85	7.40	7.94
	4.00	3.80	7.80	7.75	1.90	7.60	----

DISCUSSION.

A number of collaborators reported results by means of the Mojonnier tester. The results submitted by the collaborators are very favorable this season, also for the Roese-Gottlieb method as applied to unsweetened evaporated milk. The results on the sample of sweetened condensed milk are also quite satisfactory, although not quite so close in agreement as they were in connection with the work of 1915. If, however, the results submitted by two or three inexperienced analysts are eliminated the showing will be very satisfactory. A similar statement may be made with reference to the results submitted on ice cream. In fact, there is considerable encouragement in connection with the application of the Roese-Gottlieb method to plain ice cream. The results on dried milk and malted milk, of course, are not at all conclusive. There is good reason for a further continuance of a comparative study of the official Roese-Gottlieb method and the acid extraction method. It is believed that the difficulties inherent in this portion of the work

can be cleared up next year. At least, there is ample justification as shown by the reports of the collaborators for a continuance of this work. The results on unsweetened evaporated milk by methods of Manchester and Hunziker seem to favor the adoption of the Manchester method. It is not believed, however, that any modified Babcock test can be relied upon as a strictly accurate method for determining fat in any dairy product except whole milk, and possibly cream. Nevertheless, it is deemed desirable that a centrifugal method should be adopted as a provisional method with the understanding that the method is suitable under certain conditions for a rapid sorting-out test. There is a call for such a method in routine work in food laboratories, as well as in connection with manufacturing establishments. Results obtained by the Manchester method in the hands of experienced collaborators check quite nicely with the results obtained by the official Roese-Gottlieb method. Allowances, of course, must be made for the fact that measurements on Babcock test bottles can hardly be made closer than 0.1 per cent. Some of the collaborators report results to 0.01 per cent, but these results are obtained by averaging a number of determinations.

The Babcock test has been employed during the past quarter of a century as a satisfactory, convenient and rapid method for the determination of fat in raw milk. With evaporated milk products, however, considerable difficulty has been found in obtaining comparable results by this method. Doubtless, largely on account of the changes in the proteins, as a result of the heat of processing, the solution of the sample is rendered more difficult and the complete separation of the fat prevented. When used with products which have not been sterilized, the results may be somewhat better, but still only approximate.

Furthermore, it has long been a recognized fact that the fat column in the Babcock test contains a notable percentage of impurities, which, however, are claimed to be partly compensated for by the incomplete separation of the fat from the sample. A considerable number of the modifications of the Babcock test which have been proposed in recent years direct the use of ingredients other than sulphuric acid, thus complicating the manipulation and introducing new factors into the results. Some of these modifications require the use of amyl alcohol, others employ acetic acid, and one procedure directs the addition of a small amount of glycerol. It is obvious from a consideration of the properties of these additional reagents that the fat column is very certain to be more or less contaminated, and the measurements thereby obtained entirely too high. These facts were plainly enough illustrated by the results and comments submitted by the collaborators in 1915, and there is no disputing the conclusion, therefore, that, generally speaking, these various modifications of the Babcock test can not be sufficiently

accurate to be relied upon for the purpose of determining the per cent of fat in an evaporated milk. This statement may be rendered more emphatic by allowing no exceptions even in the case of those methods which yield a clear separation of fat and a well-defined meniscus. For the reasons above stated, it has therefore been definitely concluded to exclude these methods from further consideration. All attempts to correct for possible errors by the application of factors or to speculate more or less about compensating conditions, are quite too trivial to be entertained in connection with investigations which are supposedly based on sound principles. The two centrifugal methods which were tried out during the past season are not subject to the criticisms which have been pointed out. Nevertheless, there is a serious doubt in the minds of many of the collaborators as to whether such methods should be admitted at all, except as rapid sorting-out tests, which, of course, are frequently called for in connection with routine work. It seems advisable to recommend the adoption of a simple modification of the Babcock test to be applied to evaporated milk, with the qualification expressed in some manner that the test is designed to yield approximately reliable results under proper conditions. A comparison of the results seems to incline to a conclusion favorable to the Manchester method. In the method of Hunziker the use of a small amount of sample necessitates multiplying the fat column by a rather large factor which, at the same time, results in a corresponding multiplication of possible error. This point is a serious criticism of any analytical method. Also, generally speaking, the conditions incident to the application of the two methods are quite opposite in character. In the one case the proportion of acid to sample is comparatively small, while in the other the proportion is large; and a similar comparison may be noted with reference to the directions for mixing the sample and acid. After careful examination of all these details, the conclusion would seem to favor the method proposed by Manchester.

The Roese-Gottlieb method when applied to evaporated and condensed milk products is unquestionably accurate and is fairly satisfactory in respect to the time required for the completion of a determination. The time element involved in this method has been very greatly reduced by the mechanical device recently put upon the market by Mojonnier Bros. Co. of Chicago, Ill., and, as already stated, the method of manipulating the Mojonnier tester does not introduce any variations which are essentially different from the details of the official Roese-Gottlieb method.

In our collaborative work no attempts have been made heretofore with the application of the Roese-Gottlieb method or its modifications to samples of dried milk or malted milk. A number of analysts have

apparently acted upon the assumption that a procedure which has proved satisfactory when applied to evaporated milk products might also present no serious difficulties if carried out on products which have been reduced to a very low percentage of moisture. Various modifications of the method for the determination of fat in dried milks have for some time been under investigation by chemists, both in Europe and in America, and a number of serious problems have arisen in connection with these investigations. It has been pointed out that dried milks are likely to develop sensible quantities of free fatty acids, even when the samples are not noticeably rancid, with the result that extraction from an alkaline medium is liable to yield low results for fat. These observations were verified and pointed out in the following statement communicated by G. E. Patrick in 1915:

> The difference between results by acid and alkaline extraction is quite variable—sometimes nil, sometimes a sensible amount—and I therefore felt it best to advise the use of an acid extraction method in place of the regular Roese-Gottlieb procedure in all cases of analysis of dried milks. Naturally the same principle applies to malted milks, but to a much less degree.

The Eccher[1] method, which is only a slight modification of the Ratzlaff[2] method for cheese, has some advantages wherever much sugar is present and, doubtless owing to the lower temperature of heating with the acid, results in a cleaner separation of fat. Siegfeld[3] first made mention of a difficulty in obtaining full results for fat in old samples of dried milk, and Eccher has pointed out that, while it is impossible by the Roese-Gottlieb method to obtain good results on such samples (because of the presence of free fatty acids), correct results can be obtained by an acid extraction method which is only a slight modification of the Bondzynski[4] method for cheese. The only essential change consists in heating the sample with hydrochloric acid to 80°C. instead of to boiling temperature. This results in less carbonization and a consequently cleaner and more complete extraction. The working details of Eccher's method may be stated briefly as follows:

> Heat 1 gram of the dried milk with 10 cc. of hydrochloric acid (sp. gr. 1.125), either in a small-lipped beaker with a stirring rod or in the Röhrig tube, by means of a water bath at 80°C., for 15–25 minutes (being certain that the curd is well dissolved). Cool, add 10 cc. of alcohol, using the alcohol and the ethers in transferring to the Röhrig tube, if the heating is done in a beaker. After mixing the alcohol, add 25 cc. of ethyl ether, shake well, then follow with 25 cc. of petroleum ether, and proceed as in the Roese-Gottlieb method, making the two subsequent extractions with 15 cc. of each of the ethers as usual.

---

[1] *Arch. Chem. Mikros.*, 1913, **6**: 305.
[2] *Z. Nahr. Genussm.*, 1904, **7**: 409.
[3] *Milchwirtschaft. Zentr.*, 1910, **6**: 352.
[4] *Chem. Weekblad*, 1904 **1**: 424.

A modification of this method was later proposed by C. H. Biesterfeld, formerly of the Dairy Laboratory, Bureau of Chemistry. The details of the method may be described as follows:

To 1 gram of dried milk in a small beaker add 9 cc. of water and 2 cc. of ammonia, and stir with a rod until all lumps are disintegrated. Warm slightly to aid the solution, transfer to the extraction tube, add 10 cc. of alcohol and mix. Extract with 25 cc. portions of ethyl and petroleum ethers as in the Roese-Gottlieb method. Pass the ethers through quick-acting filters into a tared flask. Evaporate and weigh in the customary manner. Acidify the remaining extracted liquid in the Röhrig tube with 3.5 cc. of glacial acetic acid and place the tube up to the spigot in a water bath at 80°C. for about 10 minutes. By placing 2 or 3 glass beads in the bottom of the tube a quiet boiling action will be secured. Cool the tube in running water and add the alcohol to bring the volume to about the upper line of the spigot. Extract with 15 cc. each of ethyl and petroleum ether, and run off the extract in an unweighed flask. Repeat the extraction in the same manner, run off into the unweighed flask, and evaporate to dryness on the steam bath. Dissolve the small residue of fat in 10 cc. of petroleum ether. Transfer through a filter to the tared flask and wash out twice with petroleum ether. Finally, dry the total extracted fat on a warm plate, then in an oven at 120°C., and weigh.

RECOMMENDATIONS.

It is recommended—

(1) That there be a further study of modifications of the Roese-Gottlieb method applied to plain ice cream, dried milk and malted milk.

(2) That the Schmidt-Bondzynski modified method for the determination of fat in cheese be subjected to study.

(3) That the Manchester modified Babcock test be adopted as a provisional method to be applied to unsweetened evaporated milk.

REPORT ON CEREAL PRODUCTS.

By J. A. Le Clerc[1] (Bureau of Chemistry, Washington, D. C.), *Associate Referee.*

The following work was conducted:

Moisture.—Comparison of the official method with the vacuum method, using as drying agents: (b[2]) Sulphuric acid; (c) calcium chlorid; (d) calcium oxid.

Gluten.—(1) Comparison of the effect of washing the gluten until starch-free with a washing 1 minute shorter; (2) comparison of the tentative method (drying the wet gluten at 110°C. for 24 hours) with the Olson method (first heating the wet gluten at 180°C. for 15 minutes or until it springs, and then at 110°C. for 4–6 hours).

Acidity.—Comparison of the treatment of flour with water at 40°C. for 2 hours, as follows: (b[2]) Treatment with water at 40°C. for 1 hour; (c) treatment with water at 40°C. and letting mixture stand at ordinary temperature for 1 hour; (d) treatment with water at ordinary temperature for 2 hours.

---

[1] Present address, Miner-Hillard Milling Co., Wilkes-Barre, Pa.
[2] Letters "(b)", "(c)" and "(d)" in the text refer to corresponding columns in the tables.

In addition to these determinations a set of optional methods or tests was suggested and cooperation asked thereon. These included a study of the methods for the following determinations: Ash; phosphoric acid; soluble carbohydrates; cold water extract; chlorin (qualitative and quantitative). Furthermore, collaboration on two methods for making baking tests was requested.

Two samples of flour (one bleached and one unbleached) were sent to each of the 14 chemists who were expected to assist in this work. Of the reports received from 10 collaborators 8 give results for moisture, acidity, gluten and ash; 6 for phosphoric acid; 5 for soluble carbohydrates and cold water extract; 4 for chlorid and baking.

TABLE 1.

Determination of moisture.

ANALYST	(a) OFFICIAL METHOD[a]		(b) VACUUM METHOD (SULPHURIC ACID)		(c) VACUUM METHOD (CALCIUM CHLORID)		(d) VACUUM METHOD (CALCIUM OXID)	
	per cent	*time*	*per cent*	*time*	*per cent*	*time*	*per cent*	*time*
J. H. Bornmann, U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.	11.95	5½ hours	11.56	1 day	10.42	1 day	9.60	1 day
	12.24	8 hours	11.74	2 days	10.85	2 days	9.77	2 days
			11.89	3 days	10.78	3 days	9.93	3 days
			12.11	4 days	10.96	4 days	9.66	4 days
			12.07	5 days	10.97	5 days	10.56	5 days
							11.56	5 days
F. C. Atkinson, American Hominy Co., Indianapolis, Ind.	10.60		11.90		11.63		13.15 (dried in hydrogen for 6 hours)	
R. A. Thuma, University Farm, St. Paul, Minn.	12.63		12.60		12.02		12.78	
C. Kennedy, University Farm, St. Paul, Minn.	12.20	8 hours	12.45	4 days	11.85	5 days	13.22	6 days
	12.15	8 hours	13.90	4 days	11.77	5 days	13.27	6 days
W. B. Smith, Bureau of Animal Industry, Kansas City, Kans.	10.00		10.24		9.02			
	10.65		10.12		9.02			
	10.23				9.03			
	10.53				9.04			
C. R. Smith, Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	13.09		13.13		11.00			
L. H. Bailey, Bureau of Chemistry, Washington, D. C.	12.21		12.17	1 day	9.12	5 days	12.09	1 day
			12.46	2 days			12.70	5 days
			12.88	5 days				
L. Dunton, Agricultural Experiment Station, Manhattan, Kans.			10.82	5 days	8.61	3 days	10.19	3 days

[a] *Assoc. Official Agr. Chemists, Methods*, 1916, 79.

In sending out these samples no attempt was made to transport them in air-tight containers because our object was not to see if the different collaborators would find the same amount of moisture in the flour, but to see what results would be obtained by the use of the different methods in the hands of each collaborator.

MOISTURE.

(See Table 1.)

In five cases Method (a) gave results agreeing with Method (b). In two cases the results were too widely different. In every case Method (c) gave lower results than Method (b). Wherever Method (d) is compared with Method (b), the results show an encouraging agreement.

All the results given in Tables 2 to 5 are on the water-free basis.

TABLE 2.

Determination of gluten.

(On water free basis.)

ANALYST	WET			DRY		
	(a)	(b)	(c)	(a)	(b)	(c)
	Tentative method[a]	Gluten washed 1 minute less than (a)	Tentative method[a]	Dried to constant weight at 105-110°C.[b]	Dried to constant weight at 105-110°C.[b]	Dried at 180° C. for 15 minutes and to constant weight at 105-110°C.[b]
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
J. H. Bornmann	40.85	41.45	41.10	12.84	13.06	12.93
F. C. Atkinson	28.4[c]	29.5[c]	-----	9.56[c]	9.75[c]	-----
R. A. Thuma	36.4	36.7	36.6	12.72	12.82	11.67
C. Kennedy	38.30	38.56	38.14	11.78	12.18	12.29
W. B. Smith	34.95	32.95	33.7	11.20	11.00	11.20
C. R. Smith	36.8	37.7	37.7	14.0	14.0	12.9
H. L. Wessling, Bureau of Chemistry, Washington, D. C.	32.5	34.2	33.3	11.6	11.9	11.8
L. Dunton	36.7	36.6	36.7	12.25	11.94	11.63
Average	36.6	36.9	36.8	12.3	12.4	12.0

[a] *Assoc. Official Agr. Chemists, Methods*, 1916, 189.
[b] Results were obtained from corresponding column under wet gluten.
[c] Not included in average.

GLUTEN.

(See Table 2.)

The results of the gluten determination show a very good agreement between Methods (a), (b) and (c) in the hands of any one collaborator and this applies to both the wet and the dry gluten. Too much variation between results obtained by different collaborators is to be noted, however, in examining the results of any one method, e. g., Method (a) for wet gluten gives results varying from 32.5–40.8 per cent; Method (b),

34.2–41.4 per cent; Method (c), 33.3–41.1 per cent. For dry gluten Method (a) varies in the hands of the different workers from 11.2–14.0 per cent; Method (b), 11.0–14.0 per cent; Method (c), 11.2–12.9 per cent.

ACIDITY.

(See Table 3.)

No appreciable differences between the results obtained by any one collaborator are to be noted in Methods (a), (b), (c) and (d). Method (c) is the simplest, consisting of treating flour with water at 40°C. and letting the mixture stand at ordinary temperature for 1 hour with occasional shaking.

ASH.

(See Table 4.)

In eight out of nine cases the use of calcium acetate gave higher results than did the provisional method. In five of these eight cases, however, the results obtained by the use of calcium acetate are only slightly greater than those obtained by the provisional method. The results show that ashing by the provisional method is the more satisfactory and correct, provided incineration is not carried on at too high a temperature. This is evident since the results on phosphoric acid are identical when it is determined upon the ash obtained by these two methods. One must assume, therefore,

TABLE 3.

Determination of acidity.

(On water free basis.)

ANALYST	(a) METHOD OF COMMITTEE C, 1915[a]	(b) SAME AS (a) EXCEPT SAMPLES KEPT AT 40°C. FOR 1 HOUR	(c) WATER AT 40°C. ALLOWED TO STAND 1 HOUR AT ROOM TEMPERATURE	(d) SAMPLE PLUS WATER AT ROOM TEMPERATURE; ALLOWED TO STAND 2 HOURS AT ROOM TEMPERATURE
	per cent	*per cent*	*per cent*	*per cent*
J. H. Bornmann	0.109	0.113	0.110	0.098
F. C. Atkinson	0.163	0.158	0.146	0.152
R. A. Thuma	0.172	0.166	0.160	0.160
C. Kennedy	0.127	0.119	0.125	0.119
W. B. Smith	0.095	0.089	0.084	0.091
C. R. Smith	0.106	0.107	0.104	0.106
H. L. Wessling	0.137	0.134	0.131	0.129
D. H. Grant, Bureau of Chemistry, Washington, D. C.	0.133	0.125	0.120	0.116
L. Dunton	0.153	0.153	0.134	0.124
Average	0.133	0.129	0.124	0.121

[a] *J. Assoc. Official Agr. Chemists*, 1917, 3: 87.

that the results of ashing by Method (a) are better than the results obtained by Method (b) or assume that a large portion of the non-phosphoric acid material has been volatilized. The latter assumption is not logical. On the other hand it is reasonable to assume that the higher results of Method (b) are due either to incomplete incineration or to the absorption of moisture by the sample before it has been weighed.

SOLUBLE CARBOHYDRATES.

(See Table 5.)

Five reports were received. The average results from Methods (a), (b) and (c) are almost identical, i. e., 1.33, 1.38 and 1.41 per cent. In three cases Method (a) gives the lowest results; in two cases Method (b) gives the lowest results; in two cases results with Method (a) are the highest.

TABLE 4.

Determination of ash and phosphoric acid.

(On water free basis.)

ANALYST	ASH		PHOSPHORIC ACID		
	(a)	(b)	(a[a])	(b[b])	(c[c])
	Official method[d]	Calcium acetate method[e]	Official method[f]	Official method[f]	Ash heated for 1 hour in nitric acid and official method subsequently followed
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
J. H. Bornmann	0.472	0.540	0.222	0.233	0.222
F. C. Atkinson	0.442	0.570	----	----	----
R. A. Thuma	0.504	0.538	0.252	0.252	0.252
C. Kennedy	0.495	0.502	0.246	0.252	0.248
W. B. Smith	0.479	0.480	0.233	0.233	0.230
H. L. Wessling	0.478	0.490	----	----	----
L. H. Bailey	0.475	0.464	0.246	----	0.242
D. H. Grant	0.467	0.464	----	----	----
L. Dunton	0.466	0.534	0.229	0.239	0.229
Average	0.474	0.509	0.238	0.245	0.237

[a] Results in this column were obtained by determining the phosphoric acid in the ash reported by the official method, column (a) under ash.

[b] Results in this column were obtained by determining the phosphoric acid in the ash reported by the calcium acetate method, column (b) under ash.

[c] Results in this column were obtained from the ash determined by the official method, column (a) under ash.

[d] *Assoc. Official Agr. Chemists, Methods*, 1916, 187.

[e] U. S. Bur. Chem. Bull. **107**, rev.: 21.

[f] *Assoc. Official Agr. Chemists, Methods*, 1916, 3.

COLD WATER EXTRACT.

(See Table 5.)

It is evident from the reports of the collaborators that enzym action is sufficient to vitiate the results. The extraction, therefore, should be carried out at a temperature not above 10°C.

CHLORIN BLEACHED FLOUR.

Two collaborators tested for chlorin qualitatively and reported unsatisfactory results. Four collaborators reported on the quantitative determination of chlorin, two of them obtaining 26 and 27 mg., respectively, per kilogram of flour, the other two obtaining 63 and 205 mg., respectively.

TABLE 5.

Determination of soluble carbohydrates and cold water extract.

(On water free basis.)

ANALYST	SOLUBLE CARBOHYDRATES			COLD WATER EXTRACT	
	(a)	(b)	(c)	(a)	(b)
	Bryan, Given and Straughn method[a]	Sodium bicarbonate method[b]	0.5 per cent hydrochloric acid method	Ice-water	Water at room temperature saturated with toluene; kept at room temperature
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
J. H. Bornmann	1.07	1.50	1.59	5.31	7.71
R. A. Thuma	1.42	1.11	1.24	6.63	6.59
C. Kennedy	1.52	1.02	1.24	5.53	7.07
W. B. Smith	1.34	1.45	1.38	----	----
L. H. Bailey	1.32	1.86	1.60	5.81	7.15
L. Dunton	----	----	----	4.86	4.36
Average	1.33	1.38	1.41	----	----

[a] *Assoc. Official Agr. Chemists*, 1916, 109.
[b] U. S. Bur. Chem. Bull., **162**: 121.

DISCUSSION.

The lack of agreement between results obtained by different collaborators using the same methods suggests that the procedures of different analysts vary beyond the limit of error of the methods themselves. It is probable that a demonstration of the methods by one skilled in their use would be sufficient to produce more harmonious results when study of the subjects is continued.

RECOMMENDATIONS.

It is recommended—

(1) That Method (b) for the determination of moisture in flour and similar cereal products be approved; that Method (d) and Method (a) receive further study; and that Method (c) be dropped.

(2) That the method of drying wet gluten by heating to 180°C. for 15 to 20 minutes, or until it springs and then at 105° to 110°C. to constant weight (4 to 6 hours) be approved, and that work on wet and dry gluten and the washing of gluten be continued.

(3) That Method (c) for acidity be approved, and that the methods for the determination of acidity in flour receive further study.

(4) That Method (b) for ashing be approved, weighing to be made immediately upon cooling.

(5) That Method (b) for soluble carbohydrates in flour be abandoned and that Method (c) be adopted.

(6) That Method (a) for cold water extract in flour be approved.

(7) That further study be made on the testing for chlorin in bleached flour.

REPORT ON CANNED VEGETABLES.

By W. D. Bigelow (National Canners Association, 1739 H Street, Washington, D. C.), *Associate Referee on Vegetables.*

Collaborative work on canned vegetables was confined to a study of the Howard method for the microscopic examination of tomato pulp. The details of this method have been published[1]. The limitations of the method with respect to magnifications employed, character of organisms counted and similar questions were not considered. Although the importance of such questions was appreciated, it was believed that a study of the technique of the method and the promotion of uniform procedure among analysts were of more immediate importance.

In the early spring of 1916, a letter was written to all official laboratories which were known to examine tomato pulp and ketchup, and to all manufacturers and buyers of tomato pulp who were known to maintain laboratories, asking collaboration in the study of the Howard method. Encouraging response was received and eight samples were sent to each laboratory which indicated a willingness to take part in the collaborative work. Reports on at least some of the samples were received from fifty-two analysts representing thirty-eight laboratories. Of these laboratories, sixteen were official, charged with the enforcement of Federal, State and Municipal food laws; sixteen were trade laboratories, maintained by manufacturers or dealers; and seven were commercial laboratories, accustomed to examine tomato pulp for either manufacturers or dealers or both.

This work was intended to be of a preliminary nature, and collaboration was asked with the understanding that the results of the individual analysts would not be made public. The results received are given in Tables 1, 2 and 3. The laboratories and analysts are indicated by number and, where more than one analyst reported from a single laboratory, the additional analysts are indicated by letter.

CHARACTER OF EQUIPMENT USED.

Collaborators were asked to report the character of microscopic accessories they employed. Apochromatic accessories were employed by Analysts 1 to 3B, inclusive, 10, 13 and 32. All other analysts employed ordinary achromatic objectives and Huyghenian eye pieces. Those who collaborated in later work, the results of which are given in Tables 4 to 8, inclusive, were equipped with apochromatic accessories. During the season a number of the collaborating analysts brought their micro-

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 324.

scopes to the writer's laboratory and it was found that the accessories used by some would not give the necessary definition.

CONFERENCES OF ANALYSTS.

When the widely discrepant results were noted, two conferences of tomato pulp analysts were arranged, at which the analysts worked both with their own instruments and with instruments equipped with proper accessories. Much progress in uniformity was made at these conferences.

DISCUSSION OF TABLES 1, 2 AND 3.

As stated above, there are given in Tables 1, 2 and 3 the results obtained by collaborating laboratories on eight preliminary samples. These results showed the widest possible variation. For instance, on Sample A, the mold content reported by different analysts varied from 6 to 90 per cent of the fields. The bacteria count varied from 6,000,000 to 168,000,000 per cc., while the content of yeasts and spores varied from 1 to 208 per $\frac{1}{60}$ cmm. In Sample 1, the mold count varied from 4 to 100 per cent of fields, the bacteria count, from 8,000,000 to 115,000,000 per cc. and the content of yeasts and spores varied from 0 to 850 per $\frac{1}{60}$ cmm. Similar variations will be noted in the other samples given in these tables.

Of the eight samples, four were submitted to a number of laboratories in duplicate, but under different numbers. The results obtained from both examinations are given. These results illustrate the fact that good duplicates do not necessarily mean correct work. In a number of cases it will be noted that analysts whose results were far from correct checked themselves very well in examining duplicate samples, though they did not recognize them as duplicates.

COLLABORATIVE WORK WITH SAMPLES OF KNOWN CHARACTER.

During the tomato season just passed, a series of uniform samples was prepared under the personal observation of Messrs. B. J. Howard and C. H. Stephenson of the Bureau of Chemistry, and Mr. H. M. Miller of the National Canners Association. All three men were present during the manufacture of these samples and careful observation was made of the raw material and the method of manufacture. Several samples of the pulp were taken at different stages of the concentration.

From the results given in Tables 1, 2 and 3, it was obvious that nothing would be gained by having these samples examined by the entire number of collaborators. A small number of analysts was selected whose results in the preliminary work showed a reasonably good working knowledge of the method. Several analysts were also included who, it was believed

as a result of the preliminary work, had been able to correct their procedure. This list includes sixteen analysts located in twelve laboratories. Of these laboratories, four (six analysts) were official, seven (nine analysts) were trade laboratories and one (one analyst), a commercial laboratory.

The samples were examined for the purpose of securing information on the following points:

(1) Agreement between analysts working with the same samples.

(2) Relation of the concentration of pulp to the microscopic count.

(3) Relation of the microscopic count to the amount of rotting material in the raw product and hence to the perfection of sorting of the raw product.

(4) Influence of delay in manufacture on the microscopic count.

(5) Influence of the finishing operation on the microscopic count.

The conditions under which tomato pulp is manufactured vary so greatly that much difficulty is encountered in appraising the value of the Howard method for determining the presence of decomposing material, and in adopting a uniform and satisfactory procedure for interpreting the results. It was necessary, therefore, to examine a considerable number of samples prepared under different conditions of manufacture.

AGREEMENT BETWEEN ANALYSTS WORKING WITH THE SAME SAMPLES.

The results in Tables 4 to 8, inclusive, are so arranged as to give an idea of the agreement that was obtained by the sixteen analysts to whom the samples were submitted. In addition to the detailed results of the various analysts, there is given also for each sample the average of the results reported. In accordance with the custom of the association, the more extreme results have been excluded from the averages. In some cases, new samples were sent to analysts with the request that they repeat certain determinations. In such cases, the results of both determinations are given in Tables 4, 6, 7 and 8, although the results of the first examination are excluded from the averages.

In the case of Analyst 6, so many results varied greatly from those obtained by other collaborators that it was thought best to exclude all of his results from the averages.

It is pointed out, on page 458, that the count of molds does not appear to be changed by the concentration of the pulp, though the bacterial count appears to be roughly proportional to the concentration. The agreement between analysts in mold count, therefore, can be studied

advantageously in Table 4, while the bacterial count can be studied better in Table 5, not taking into consideration those figures that are excluded from the averages.

The detailed figures for mold count in Table 4 are especially interesting. In Series 1 and 2, in which the average mold count is 29 and 18, respectively, results of the individual analysts rarely vary from the average by as much as 10. While an error of this magnitude is material when considered on a percentage basis, it becomes insignificant when we consider the purpose of the method and that a mold count of 66 per cent is permitted. The samples mentioned represent good average pulp, and the reports from the individual collaborators show that there is no probability of their mistaking a pulp of this nature for a pulp containing molds in 66 per cent of the fields.

With Series 3 and 4, the case is somewhat different. The samples in Series 3 have a mold count of about 50. Two of the analysts reported results, on one sample each, as high as 66 per cent of the fields. Samples in Series 4 have a mold count of about 65. A variation of 10 either way from this figure, that is, a range of from 55 to 75, would include a great majority of the results received, yet several collaborators reported results outside of this range. For instance, Analysts 4 and 8 reported results as low as 40 and 41, while Analysts 5, 8 and 10 reported results as high as 86 and 87.

The individual results obtained by all analysts from the various samples of each series agree with each other much more closely than do the results of the various analysts. For instance, Analyst 10, who obtained the highest results, had a range of from 73 to 87; Analyst 5, whose results were also high, had a range of from 71 to 86; Analyst 8, whose results were the lowest, had a range of from 40 to 54.

It should be borne in mind that the samples were all submitted to the collaborators by number, and it was not possible for any collaborator to know that the samples of any series were in any way related to each other. It is therefore obvious that, with more intensive work and more frequent checking between the different collaborators, the variation in the results of different analysts would more nearly approach the variation in the results of one analyst from the examination of a single series of samples.

In Table 6 the variation between the mold count of the different analysts was similar in a general way to Series 3 and 4 of Table 4. The results given in this table show that, working with a limit of 66, analysts of experience in the method are likely to condemn a sample of pulp whose correct mold count is as low as 50. Just how much of this is due to inaccuracy of the method and how much to personal equation, it is impossible to say at this time.

Under present conditions, therefore, it is obvious that, with a limit of 66, a sample which an individual analyst finds to contain molds in more than 50 per cent of the fields is in the danger zone. It is also obvious that in taking action on a sample whose mold count is not greatly in excess of 66, it is necessary for an official analyst to examine several samples, or to make a number of independent examinations of the same sample.

The results of individual collaborators on bacterial counts on Series 1 to 4, inclusive, of Tables 4 and 5, show that, when working with samples with a low bacterial count, experienced analysts should reach the same conclusion, although the percentage of variation may be extremely large. With a somewhat higher bacterial count, the percentage of variation appears to decrease.

With a high bacterial count, such as results from allowing tomato pulp to stand for a number of hours in process of manufacture, it appears that the difficulty of distinguishing the organisms from other bodies of microscopic size is greatly increased. This increases, in turn, the error of the method and the variations in the results of different analysts. It is the experience of the writer's laboratory that, as in the case of molds, much greater uniformity can be obtained in the bacterial count by a careful study of the method. At the same time, the increase in bacteria is accompanied by the disintegration of the cells and the formation of debris to such an extent that an accurate count is difficult. This difficulty can be overcome to a certain extent by dilution of the sample, but this, in turn, introduces a proportional multiplication of error. In using the method, therefore, it must be kept in mind that the present working limits were adopted with the belief that they were really excessive and with a view to making allowance for error of method, variation in sample and personal equation of analysts. Great care should be taken, therefore, in the interpretation of results which approach closely the limit mentioned.

Official analysts will be wise to confirm very carefully bacterial counts which are not far above the limit of 100, and manufacturers should view with suspicion batches of pulp whose bacterial count is reported to them as over 80. When the bacterial count greatly exceeds 100, the variation between the results of two analysts or between the results on the same sample by the same analyst increases enormously. This is doubtless partly because analysts have not given much attention to the exact count of pulps that were obviously far beyond the limit. As stated elsewhere, this difficulty can probably be overcome to a certain extent by increased dilution of the samples counted.

It is unfortunate that the samples examined did not include some that were high in yeasts and spores. The maximum number of yeasts

and spores permitted by the Bureau of Chemistry is 125 per $\frac{1}{60}$ cmm. The average yeast and spore counts of the samples included in Tables 4 to 8 varied from 6 to 27. In general it may be stated that the variation of the individual collaborators in the yeast and spore count was similar to the variation in the bacteria count in Series 1 to 4, inclusive, of Table 4, and in Tables 6 and 8. It is hoped that the work will be continued and a comparative study made of a series of samples with a relatively high content of yeasts and spores.

RELATION OF THE CONCENTRATION OF PULP TO THE MICROSCOPIC COUNT.

In Table 4 are given results obtained by the Howard method on eight series of samples of tomato pulp taken at various stages of concentration. The first sample in each series represents the unconcentrated pulp just as it flowed from the cyclone. The succeeding samples in each series were taken from the same kettle as the first sample, at varying degrees of concentration, the extent of which is indicated by the per cent of solids. The influence of concentration on the microscopic count is best shown by a comparison with each other of the average figures of the samples in each series for molds, bacteria, and yeasts and spores, respectively. The mold count is strikingly uniform throughout the various stages of concentration.

The bacterial count in the first four series is also uniform throughout the different stages of concentration. In the last four series, the bacterial count increases with increased concentration. It appears altogether probable that the lack of increase noted in the first four series with increasing concentration may have been due to the fact that the number of organisms present was no greater than the error of the method.

In Table 5, the bacterial count of the various samples in each series is calculated to pulp of 8.37 per cent solids. This percentage of solids is equivalent to a specific gravity of 1.035, which is the concentration most commonly demanded in the trade. Although there are a few striking exceptions, the uniformity in general is so great as to suggest that the bacterial count is directly proportional to the concentration of the pulp.

It will be noted that, as a rule, the average result on the first sample in each series is higher than the others. This is probably due to the fact that, in the first sample of each series, the dilution which was counted was of lower concentration than in the case of the other samples. Consequently, there were fewer particles of all kinds in each small square of the microscopic field and these particles were identified and counted more easily and with greater accuracy. This suggested the thought that more accurate results might be obtained by diluting highly con-

centrated pulps and pastes further than is called for in the Howard method, and subsequent experimental work in the writer's laboratory has established the wisdom of this procedure. It is believed that to obtain the best results the samples should be diluted to such an extent that the small squares will contain less than 10 bacteria each. In case the field shows considerable debris the sample should be still further diluted. In this way the error of the determination is greatly increased by the factor with which the microscopic reading must be multiplied. This error is more than compensated, however, by increased accuracy in identifying the organisms in the field.

The results obtained from the determination of yeasts and spores, as shown in Table 4, do not indicate an increase in the number of yeasts and spores with increased concentration of the pulp. It is unfortunate, however, that all of the samples taken were so low in yeasts and spores that it is entirely possible that the error of the determination would be sufficient to conceal a greater number of those bodies in the higher concentration.

It is pointed out above that, in the first four series in Table 4, which were very low in bacteria, the bacterial count is practically uniform in all stages of concentration, while in the last four series, which were high in bacteria, the bacterial count is practically proportional to the concentration. The fact that the yeast and spore count, which is low in all samples, is practically the same for all stages of concentration, therefore, does not warrant the inference that uniformity would obtain with different stages of concentration of a sample high in yeasts and spores.

RELATION OF MICROSCOPIC COUNT TO THE AMOUNT OF ROTTING MATERIAL IN THE RAW PRODUCT.

It is well known that the particles of mold disclosed by the microscope in the examination of a sample of pulp come from several sources. Mold sometimes clings in considerable quantity to the outside of tomatoes. While by far the greater proportion of this is removed by washing the tomatoes, undoubtedly some particles remain and are found in the pulp. Again, in view of the minute particles into which the mold is broken in the manufacture of pulp, if all the appliances with which the mold comes into contact are not kept scrupulously clean there is a possibility of the amount of mold in the finished product being increased from that source. By far the greater part of the mold particles in tomato pulp, however, comes from rotting portions of the tomatoes from which it is manufactured, and it is believed that, if it were possible to remove every particle of rot from the raw product, the mold content of the finished pulp, made with reasonable care in washing and sorting and reasonable cleanliness of the plant, would be very low.

It is obviously impossible to remove every particle of mold from the raw product. Even if perfection were attainable in trimming the outside of the tomatoes, it sometimes happens that a mass of mold is found in the center of the tomato with no mark on the outside to indicate its presence. It becomes a matter of importance, therefore, to determine to what extent the mold count of the finished product is an indication of efficiency in sorting and in the elimination of rot.

To study this question, it was planned to visit a number of plants during the season and to take samples from typical batches of pulp, carefully inspecting the raw product from which they were made and determining the percentage of rotting material in each. Unfortunately, time did not permit this work to be done to the extent that was planned. Only nine samples were put up in this manner, and they consisted entirely of trimming-stock pulp; that is, pulp prepared from the peelings and cores of the tomato cannery. Since in canning tomatoes there is not far from 50 per cent of waste, the amount of trimming-stock pulp made from a ton of tomatoes is something less than one-half (probably not far from 40 per cent) of the amount that would be made from a ton of whole tomatoes. Since the rotting portions of tomatoes are almost all on the outside, practically all of the decomposing material of the tomatoes will be included in the trimming-stock pulp, so that from the same tomatoes the amount of decomposing material in trimming-stock pulp is probably about two and one-half times the amount in pulp made from whole tomatoes. Therefore, if the figures given in the column headed "Rot in Tomatoes", in Table 6 be multiplied by the factor 2.5, they will probably approximate the percentage which the rotting portions would constitute of the trimming stock from which the pulp was made.

The results shown in Table 6 are too meagre and are not sufficiently consistent to enable any conclusion to be drawn as to the relation between the amount of rotting material in the raw product and the mold count of trimming-stock pulps. In a general way it would appear that the mold count of samples made from material containing a larger amount of rot was higher than in samples made from material containing a smaller amount of rot. It is regretted that the volume of the work is not sufficient to permit a more definite conclusion.

It should be remembered that the determination of rotting material is complicated by the fact that, in order to remove all of the rotting portions of the tomatoes, it is necessary to cut out a relatively large amount of sound material. Undoubtedly, therefore, the figure given in the column headed "Per Cent Rot" is only an approximation of the amount of tomatoes that must be discarded in removing the rot. In order to determine the amount of rotting material in the raw product,

the tomatoes from whose trimmings each batch was made were sampled on the sorting belt after passing the sorters. To prevent the possibility of selection, the samples were taken by removing a shovelful at a time from the belt at frequent intervals. It was assumed that the samples so taken represented the entire batch. From these samples, the rotting material was cut out as neatly as possible, the trimmed tomatoes and the rotting portions were weighed separately and the percentage of rot was calculated.

The batches of pulp made from the tomatoes so sampled were sealed in cans, processed in the usual way and samples taken for analysis.

INFLUENCE OF DELAY IN MANUFACTURE ON THE MICROSCOPIC COUNT.

When supplied with suitable medium, it is well known that bacteria increase with remarkable rapidity. When tomato pulp is found with a high bacterial count, the reason is sought first in delay at some stage of the manufacture of the product. It is obvious that the increase in number of bacteria will depend on many conditions which are more or less susceptible of control. The variation from plant to plant and even from day to day in the same plant is so great that it could hardly be said that any individual illustration would be typical. It was thought to be of interest, however, to call attention to one sample of pulp which was allowed to stand all day in the factory for the purpose of observing the microscopic count at intervals. The results of this work are shown in Table 7. Unfortunately, the fresh sample, whose bacterial count would doubtless have been very low, was not sampled. After Sample 26 was sterilized, the remainder of the batch was allowed to stand 6 hours, when a portion of it was removed, sterilized and numbered 28, the remainder being allowed to stand 4 hours longer, when it was sterilized and numbered 36.

INFLUENCE OF THE FINISHING OPERATION ON THE MICROSCOPIC COUNT OF TOMATO PULP.

The screen used in an ordinary cyclone employed for straining unconcentrated tomato pulp from the peelings and seeds permits many black specks, consisting of particles of discolored stems, calyx and black mold, to pass through with the pulp. To remove these and improve the consistency of the product, many manufacturers employ a finishing machine, which is provided with a much finer screen than the cyclone. The influence of this screen on the microscopic count of tomato pulp has often been a matter of discussion. Some believe that the fine screen tears to pieces clumps of bacteria so that they can be seen more readily,

and divides pieces of mold into a number of smaller particles so that they are distributed among several microscopic fields. Some, on the other hand, believe that the finishing machine does not change the bacterial count and that, by removing the clumps of hard rot, it actually reduces the mold count.

For a study of this matter, six batches of pulp which were being manufactured in six different canneries were made the subject of study and samples of each were taken both before and after finishing. The results are given in Table 8. It will be noted that the microscopic count of the unfinished samples and the finished samples is practically identical.

CONCLUSIONS.

The most striking lesson from the work presented here is that the majority of analysts who profess to use the Howard method are not familiar with it; the method is purely arbitrary and an analyst can not expect to obtain satisfactory results without being personally trained by one accustomed to use the method. It is necessary that the microscopic accessories be well adapted to the method. It is the experience of the writer's laboratory that from two weeks to a month of consecutive work under the personal direction of an experienced man is necessary to train an analyst in the use of this method, and that constant practice is necessary to retain a working knowledge of it. Of still greater importance is the aptitude of the analyst. The method is not one that all can learn to use.

In a method of this nature it can not be hoped that duplicate readings can be obtained which will have as much uniformity as is expected in analytical chemistry.

Judging by the results obtained, it is important that a number of samples be examined from a given lot of pulp or that a number of independent counts be made on it before conclusion is drawn. Working with the standard of 100 million bacteria per cc. and molds in 66 per cent of fields, it would appear from the results obtained that official analysts should check their work carefully before taking action regarding pulp which only slightly exceeds those limits and that manufacturers, on the other hand, should view with suspicion any pulp whose bacterial count exceeds 80 million per cc. or which shows mold in more than 50 per cent of the fields. In this connection it should be noted that the figures given in Tables 1, 2 and 3 amply demonstrate that no credence should be given to the work of analysts who have not had personal instruction from one skilled in the use of the method.

The yeast and spore content of the samples examined was so low in all cases that no conclusion can be drawn regarding the ability of experienced analysts to check each other in samples whose yeast and spore count is relatively high.

In the concentration of pulps, the mold count is not increased, but the increase in the bacterial count is probably proportional in a general way to the concentration. This increase was not demonstrated in the samples of low bacterial count, but was evident in the samples high in bacteria. It seems probable, therefore, that the fact that it was not demonstrated by the samples low in bacteria was due rather to difficulty in counting the more concentrated pulps in each series than to the fact that the increase did not occur.

Unfortunately, the series of tomato pulps low in bacteria were not concentrated to a heavy paste and the data secured on the concentration of pulps of this nature is therefore not complete.

Delay in the operation of manufacture of tomato pulp may, in some instances at least, cause great increase in bacterial count. The operation known as "finishing" (straining through a very fine mesh screen) does not increase the count of bacteria, mold or yeast and spores.

NOTE.—Throughout these tables, where more than one determination is reported on the same sample by one analyst, a duplicate sample was sent him, without his knowledge of its nature, for the purpose of checking the first determination.

TABLE 1.

Mold count of tomato pulps.

(Expressed as per cent of fields showing molds.)

ANALYST	SAMPLE A	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7
1	57	53	60	60	67	51	--	24
1A	62	61	68	55	72	44	17	30
2	57	45	82	75	79	61	10	38
3	60	52	70	63	75	56	30	27
3A	56	46	70	66	80	60	30	37
3B	54	44	76	50	42	54	--	24
3B	--	54	--	--	--	--	--	--
4	60	40	60	52	64	53	16	28
4	--	44	56	--	--	--	--	27
5	83	48	69	60	70	52	12	38
5	--	55	76	--	--	--	--	40
5A	82	42	79	65	75	53	18	31
5A	--	62	79	--	--	--	--	38
6	25	64	70	56	32	49	23	33
7	63	36	80	30	98	32	12	12
8	68	36	52	50	52	42	8	18
8	--	40	46	--	--	--	--	18
9	30	49	49	62	41	69	20	30
10	62	50	66	55	65	58	15	36
10	--	49	69	--	--	--	--	23
11	56	--	--	--	--	--	--	--
12	54	20	78	28	58	52	4	32
12	--	24	68	--	--	--	--	32
13	60	50	64	52	38	44	14	26
13	--	52	62	--	--	--	--	32
14	63	66	93	66	74	76	42	36
14A	65	78	81	79	86	72	40	36
15	80	26	84	46	54	44	12	28
16	12	24	20	10	14	30	4	4
17	70	35	55	32	58	30	20	30
18	90	--	--	--	--	--	--	--
18A	83	--	--	--	--	--	--	--
19	--	48	42	46	46	38	18	14
19A	--	36	44	36	38	38	26	28
19B	--	46	56	30	34	44	16	20
20	11	8	8	7	15	12	6	7
20	--	4	20	--	--	--	--	8
21	76	54	--	39	--	--	--	10
21	--	52	--	--	--	--	--	16
22	--	8	30	10	--	--	--	--
23	49	--	--	--	--	--	--	--
24	41	--	--	--	--	--	--	--
25	25	35	--	30	--	--	--	50
25	--	35	--	--	--	--	--	50
26	6	--	--	--	--	--	--	--

TABLE 1.—Concluded.

ANALYST	SAMPLE A	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7
27	65	70	26	49	60	35	12	25
28	8	16	66	36	86	28	6	6
28	--	--	--	--	--	--	8	--
29	72	47	63	52	62	34	--	29
29	--	46	37	--	--	--	--	28
29A	29	38	52	50	42	34	8	28
29A	--	38	36	--	--	--	--	24
30	29	--	--	--	--	--	--	--
31	7	80	--	50	--	--	--	46
31	--	60	--	--	--	--	--	20
32	80	48	--	46	--	--	--	36
32	--	32	--	--	--	--	--	10
32A	--	44	--	49	--	--	--	27
32A	--	36	--	--	--	--	--	20
33	36	--	--	--	--	--	--	--
33A	52	--	--	--	--	--	--	--
34	70	64	--	--	--	--	--	--
35	35	38	--	44	--	--	--	10
35	--	36	--	--	--	--	--	12
36	79	--	--	--	--	--	--	--
36A	--	61	--	58	--	--	--	47
36A	--	61	--	--	--	--	--	43
36B	--	61	--	55	--	--	--	51
36B	--	48	--	--	--	--	--	42
36C	--	63	--	58	--	--	--	60
36C	--	51	--	--	--	--	--	48
37	9	60	60	70	50	68	32	40
38	--	100	--	--	--	--	--	--
Correct count[a]	57	53	70	60	72	53	20	28

[a] By correct count is meant the count which it is believed will be obtained by the careful application of the Howard method. It is the average count obtained by six analysts who appeared to be most conversant with the method.

TABLE 2.

Bacterial count of tomato pulps.

(Expressed as million bacteria per cc.)

ANALYST	SAMPLE A	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7
1	32	17	28	31	45	340	--	20
1A	33	20	22	32	57	409	12	30
2	40	40	19	46	85	500	3	39
3	34	15	72	22	62	240	3	17
3A	22	17	69	23	54	216	4	15
3B	26	15	65	26	52	176	--	11
3B	--	19	--	--	--	---	--	--
4	26	24	24	40	86	144	6	12
4	--	21	29	--	--	---	--	38
5	17	22	22	10	26	24	--	19
5	--	12	26	--	--	---	--	17
5A	15	31	17	14	31	58	12	19
5A	--	8	19	--	--	---	--	32
6	17	26	23	27	23	37	22	42
7	48	20	40	40	100	1000	25	40
8	34	16	37	38	49	178	12	20
8	--	29	38	--	--	---	--	26
9	12	36	96	60	53	120	29	60
10	84	31	26	32	69	271	19	40
10	--	30	69	--	--	---	--	40
11	76	--	--	--	--	---	--	--
12	86	28	50	59	43	160	7	27
12	--	37	24	--	--	---	--	30
13	27	12	60	20	60	125	12	20
13	--	20	20	--	--	---	--	16
14	56	115	530	168	176	362	108	101
14A	29	23	91	14	19	35	7	13
15	31	21	24	29	50	216	7	17
16	10	27	194	132	77	86	75	93
17	24	26	54	34	80	180	8	43
18	96	--	--	--	--	--	--	--
18A	22	--	--	--	--	---	--	--
19	--	20	67	76	96	136	21	69
19A	--	25	52	61	57	181	108	42
19B	--	59	97	191	73	72	26	80
20	36	64	41	36	113	86	14	36
20	--	38	37	--	--	---	--	31
21	168	77	--	139	--	---	--	19
21	--	34	--	--	--	---	--	115
22	--	8	72	19	--	---	--	--
23	43	--	--	--	--	---	--	--
24	126	--	--	--	--	---	--	--
25	30	30	--	44	--	---	--	38
25	--	30	--	--	--	---	--	36
26	24	--	--	--	--	---	--	--
27	6	13	14	72	31	240	13	5

TABLE 2.—Concluded.

ANALYST	SAMPLE A	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7
28	50	43	283	172	132	216	96	158
29	48	12	19	18	55	115	3	67
29	--	13	48	--	--	---	--	96
29A	40	8	24	16	34	96	14	57
29A	--	12	49	--	--	---	--	96
30	40	--	--	--	--	---	--	--
31	17	15	--	62	--	---	--	53
31	--	22	--	--	--	---	--	21
32	46	24	--	35	--	---	--	44
32	--	35	--	--	--	---	--	44
32A	--	23	--	32	--	---	--	35
32A	--	25	--	--	--	---	--	43
33	7	--	--	--	--	---	--	--
33A	10	--	--	--	--	---	--	--
34	67	31	--	--	--	---	--	--
35	17	36	--	36	--	---	--	104
35	--	48	--	--	--	---	--	38
36	61	--	--	--	--	---	--	--
36A	--	41	--	61	--	---	--	43
36A	--	29	--	--	--	---	--	50
36B	--	35	--	50	--	---	--	49
36B	--	30	--	--	--	---	--	34
36C	--	38	--	67	--	---	--	41
36C	--	44	--	--	--	---	--	67
37	10	18	30	18	31	34	10	16
38	--	34	--	--	--	---	--	--
Correct count[a]	32	17	50	30	55	250	8	20

[a] By correct count is meant the count which it is believed will be obtained by the careful application of the Howard method. It is the average count obtained by six analysts who appeared to be most conversant with the method.

TABLE 3.

Yeast and spore count of tomato pulps.

(Expressed as number of yeasts and spores per $\frac{1}{60}$ cmm.)

ANALYST	SAMPLE A	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7
1	30	28	15	12	75	10	--	17
1A	22	26	12	12	71	13	13	14
2	38	54	20	20	87	20	7	46
3	28	30	18	15	72	20	6	18
3A	20	35	24	20	64	36	7	20
3B	26	30	28	22	70	10	--	10
3B	--	34	--	--	--	--	--	--
4	34	21	21	30	148	20	8	20
4	--	64	21	--	--	--	--	33
5	13	40	22	55	60	38	--	135
5	--	121	12	--	--	--	--	33
5A	12	40	29	50	50	41	16	133
5A	--	131	17	--	--	--	--	70
6	16	40	16	48	18	30	18	28
7	110	43	29	3	83	--	7	8
8	32	35	10	10	46	18	4	18
8	--	26	12	--	--	--	--	24
9	12	44	28	38	36	30	24	32
10	18	20	10	14	96	28	6	32
10	--	10	29	--	--	--	--	12
11	32	--	--	--	--	--	--	--
12	35	376	30	27	49	23	8	130
12	--	--	31	--	--	--	--	53
13	43	12	9	12	54	6	6	24
13	--	20	5	--	--	--	--	16
14	62	166	142	27	65	88	21	40
14A	142	200	147	83	100	45	30	43
15	36	20	12	11	56	14	8	21
16	2	26	5	5	34	5	7	1
17	--	62	25	32	130	22	9	33
18	20	--	--	--	--	--	--	--
18A	106	--	--	--	--	--	--	--
19	--	82	29	52	69	76	22	112
19A	--	101	85	127	99	154	98	255
19B	--	138	58	130	96	84	33	150
20	28	57	18	28	114	28	12	33
20	--	49	12	--	--	--	--	22
21	34	70	--	30	--	--	--	10
21	--	20	--	--	--	--	--	36
22	--	22	119	23	--	--	--	--
23	60	--	--	--	--	--	--	--
24	6	--	--	--	--	--	--	--
25	18	20	--	20	--	--	--	24
25	--	18	--	--	--	--	--	18
26	5	--	--	--	--	--	--	--

TABLE 3.—Concluded.

ANALYST	SAMPLE A	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4	SAMPLE 5	SAMPLE 6	SAMPLE 7
27	25	175	2	16	110	20	20	120
28	4	0	0	0	3	0	0	0
29	25	39	8	14	61	9	4	12
29	--	13	8	--	--	--	--	12
29A	30	34	11	14	33	12	16	10
29A	--	16	27	--	--	--	--	14
30	30	--	--	--	--	--	--	--
31	24	38	--	39	--	--	--	28
31	--	41	--	--	--	--	--	22
32	46	26	--	13	--	--	--	11
32	--	25	--	--	--	--	--	12
32A	--	37	--	17	--	--	--	32
32A	--	33	--	--	--	--	--	30
33	208	--	--	--	--	--	--	--
33A	30	--	--	--	--	--	--	--
34	84	112	--	--	--	--	--	--
35	25	36	--	12	--	--	--	15
35	--	55	--	--	--	--	--	22
36	61	--	--	--	--	--	--	--
36A	--	31	--	19	--	--	--	26
36A	--	38	--	--	--	--	--	27
36B	--	32	--	--	--	--	--	35
36B	--	32	--	--	--	--	--	28
36C	--	36	--	30	--	--	--	34
36C	--	38	--	--	--	--	--	32
37	1	850	500	200	48	16	10	14
38	--	60	--	--	--	--	--	--
Correct count[a]	30	30	18	15	72	20	10	17

[a] By correct count is meant the count which it is believed will be obtained by the careful application of the Howard method. It is the average count obtained by six analysts who appeared to be most conversant with the method.

TABLE

Microscopic count of samples taken at different stages of the

DETERMINATION	SAMPLE NUMBER	SOLIDS	ANALYST						
			1	1A	2	3	3A	4	5
SERIES 1.									
	9	*per cent* 4.96							
Molds[a]	--	----	20	34	32	24	25	21	32
Bacteria[b]	--	----	19	18	20	12	23	13	7
									2[d]
Yeasts and spores[c]	--	----	7	9	5	2	12	9	7
	10	5.88							
Molds[a]	--	----	--	14	--	30	18	19	28
Bacteria[b]	--	----	--	4	--	19	20	14	6
Yeasts and spores[c]	--	----	--	3	--	8	12	13	8
	11	7.34							
Molds[a]	--	----	--	30	--	34	22	24	--
Bacteria[b]	--	----	--	10	--	17	16	14	--
Yeasts and spores[c]	--	----	--	4	--	6	10	6	--
	12	10.58							
Molds[a]	--	----	30	40	40	36	31	26	42
Bacteria[b]	--	----	26	22	26	19	15	17	9
									10[d]
Yeasts and spores[c]	--	----	13	13	15	5	8	4	18
SERIES 2.									
	14	5.00							
Molds[a]	--	----	8	12	10	20	16	9	17
								10[d]	
Bacteria[b]	--	----	5	4	4	7	11	18	8
						22[d]	25[d]	26[d]	
Yeasts and spores[c]	--	----	5	2	3	6	8	4	7
								7[d]	
	15	8.58							
Molds[a]	--	----	--	12	--	24	32	--	--
Bacteria[b]	--	----	--	5	--	5	13	--	--
Yeasts and spores[c]	--	----	--	5	--	11	24	--	--
	16	15.22							
Molds[a]	--	----	26	20	--	26	24	6	33
								7[d]	
Bacteria[b]	--	----	19	18	--	34	28	15	22
								26[d]	
Yeasts and spores[c]	--	----	14	8	--	14	10	9	17
								6[d]	

[a] Expressed as per cent of microscopic fields showing molds.
[b] Expressed as million bacteria per cc.

4.

concentration of individual batches of tomato pulp.

ANALYST									AVERAGE
5A	6	8	10	12	13	14	14A	15	
SERIES 1.									
28	38[d]	24	24	28	30	30	28	--	27
3	9[d]	21	12	10	15	5	7	--	13
3[d]									
8	22[d]	5	5	--	4	8	6	--	7
--	24[d]	22	--	--	26	40	26	--	25
--	27[d]	10	--	--	12	3	5	--	10
--	235[d]	7	--	--	10	4	6	--	8
33	--	22	--	--	34	40	34	--	30
14	--	11	--	--	10	10	6	--	12
16	--	110[d]	--	--	8	8	7	--	8
40	26[d]	26	29	26	36	--	--	--	34
11	16[d]	13	10	14	19	--	--	--	17
7[d]									
22	37[d]	12	3	--	12	--	--	--	11
SERIES 2.									
13	30[d]	12	13	6	6	10	32	12	13
					12[d]			12[d]	
5	15[d]	8	9	5	14	5	4	10	8
					17[d]			24[d]	
12	16[d]	1	1	10	2	6	12	3	5
					5[d]			4[d]	
19	36[d]	12	--	4	14	16	24	12	17
12	36[d]	18	--	8	10	4	3	24	10
6	80[d]	6	--	4	5	8	3	4	8
26	28[d]	10	--	10	24	22	34	20	22
					22[d]				
19	46[d]	22	--	6	32	4	12	24	20
					30[d]				
14	105[d]	6	--	3	7	10	7	13	10
					8[d]				

[c] Expressed as number of yeasts and spores per $\frac{1}{25}$ cmm.
[d] Not included in average.

TABLE

DETERMINATION	SAMPLE NUMBER	SOLIDS	ANALYST						
			1	1A	2	3	3A	4	5
SERIES 3.									
	21	*per cent* 5.03							
Molds[a]	--	----	49	60	51	56	46	37[d] 27[d]	47
Bacteria[b]	--	----	7	5	13	14	14	12[d] 14[d]	15
Yeasts and spores[c]	--	----	15	11	11	20	16	13 18[d]	20
	41	6.12							
Molds[a]	--	----	--	42	--	56	44	25[d]	--
Bacteria[b]	--	----	--	10	--	14	7	17	--
Yeasts and spores[c]	--	----	--	9	--	20	20	17	--
	42	8.81							
Molds[a]	--	----	--	54	--	54	54	23[d]	60
Bacteria[b]	--	----	--	7	--	17	12	17	7
Yeasts and spores[c]	--	----	--	10	--	18	20	23	21
	25	13.17							
Molds[a]	--	----	--	42	--	55	46	18[d]	59
Bacteria[b]	--	----	--	12	--	29	22	14	25
Yeasts and spores[c]	--	----	--	23	--	32	26	24	36
SERIES 4.									
	47	5.47							
Molds[a]	--	----	--	53 58[d]	--	58	57	52	--
Bacteria[b]	--	----	--	14 7[d]	--	14	17	24	--
Yeasts and spores[c]	--	----	--	7 5[d]	--	22	16	12	--
	22	6.35							
Molds[a]	--	----	66	63 84[d]	71	60	56	48 43[d]	68
Bacteria[b]	--	----	7	11 7[d]	12	10	8	13 12[d]	19
Yeasts and spores[c]	--	----	10	3 9[d]	7	9	12	18 11[d]	23
	45	8.39							
Molds[a]	--	----	--	63 56[d]	--	62	58	--	--
Bacteria[b]	--	----	--	11 7[d]	--	14	14	--	--
Yeasts and spores[c]	--	----	--	13 8[d]	--	24	16	--	--
	46	9.70							
Molds[a]	--	----	--	66 72[d]	--	68	64	41	78 90[d]
Bacteria[b]	--	----	--	13	--	24	29	14	18
Yeasts and spores[c]	--	----	--	7	--	46	16	21	35

[a] Expressed as per cent of microscopic fields showing molds.
[b] Expressed as million bacteria per cc.

4.—Continued.

ANALYST									AVERAGE
5A	6	8	10	12	13	14	14A	15	
SERIES 3.									
52	42[d]	36	66	6[d]	52 58[d]	66	60	46	53
22	18[d]	18	12	10	15 24[d]	4	5	24	13
18	16[d]	9	8	10	8 16[d]	10	13	7	13
58	28[d]	--	--	--	64	50	52	--	52
12	26[d]	--	--	--	12	4	5	--	10
15	75[d]	--	--	--	10	12	16	--	15
--	51[d]	36	--	14[d]	66	40	44	--	51
--	45[d]	29	--	13	8	3	4	--	12
--	48[d]	16	--	10	14	9	12	--	15
60	28[d]	34	65	30[d]	60 26[d]	50	62	--	54
17	65[d]	27	21	24	24 36[d]	7	6	--	19
30	1000[d]	28	8	6	13 18[d]	49	50	--	27
SERIES 4.									
72	58[d]	52	73	20[d]	64	64	66	--	60
5	38[d]	28	15	13[d]	24	12	25	--	18
11	55[d]	9	10	2[d]	7	20	31	--	15
71	76[d]	42	78	22[d]	56 60[d]	76	72	68	64
17	60[d]	24	28	6[d]	12 5[d]	8	4	17	14
16	74[d]	12	8	10[d]	10 9[d]	24	10	12	12
75	76[d]	54	78	28[d]	72	68	60	56	65
9	24[d]	35	13	5[d]	12	2	2	12	14
10	128[d]	14	10	9[d]	10	16	20	6	14
86 88[d]	78[d]	40	87	46[d]	64 62[d]	--	--	48	66
19	32[d]	10	16	14[d]	20 40[d]	--	--	14	18
36	400[d]	12	12	10[d]	15 12[d]	--	--	7	22

[c] Expressed as number of yeasts and spores per $\frac{1}{50}$ cmm.
[d] Not included in average.

TABLE

DETERMINATION	SAMPLE NUMBER	SOLIDS	ANALYST						
			1	1A	2	3	3A	4	5
SERIES 5.									
	26	*per cent* 5.33							
Molds[a]	--	----	--	6	--	20	22	18	20
Bacteria[b]	--	----	--	62	--	84	89	210[d]	100
						79[d]	91[d]		36[d]
Yeasts and spores[c]	--	----	--	1	--	1	4	5	20
	29	12.98							
Molds[a]	--	----	--	16	--	24	14	8	16
Bacteria[b]	--	----	--	172	--	437	270	504[d]	226
				125[d]					
Yeasts and spores[c]	--	----	--	6	--	14	6	12	6
SERIES 6.									
	31	17.20							
Molds[a]	--	----	--	10	--	16	12	--	10
Bacteria[b]	--	----	--	442	--	724	435	--	840
				400[d]					
Yeasts and spores[c]	--	----	--	18	--	14	8	--	20
	27	22.60							
Molds[a]	--	----	--	14	14	22	3[d]	--	40
Bacteria[b]	--	----	--	662	821	720	1750[d]	--	880
				636[d]					
Yeasts and spores[c]	--	----	--	12	6	10	9[d]	--	28
SERIES 7.									
	28	5.00							
Molds[a]	--	----	--	10	--	22	20	3[d]	28
Bacteria[b]	--	----	--	357	--	451	415	990[d]	420
				338[d]					
Yeasts and spores[c]	--	----	--	2	--	4	6	4[d]	15
	32	8.42							
Molds[a]	--	----	--	10	--	10	10	--	18
Bacteria[b]	--	----	--	703	--	713	700	--	1100[d]
				615[d]			960[d]		
Yeasts and spores[c]	--	----	--	6	--	4	18	--	24
	33	14.07							
Molds[a]	--	----	--	8	--	12	13	--	12
Bacteria[b]	--	----	--	720[d]	--	1656	1620	--	1000
				765[d]					
Yeasts and spores[c]	--	----	--	4	--	6	15	--	24
	34	17.83							
Molds[a]	--	----	--	18	--	18	13	--	18
Bacteria[b]	--	----	--	1180	--	1857	1700	--	1500
						3520[d]			
Yeasts and spores[c]	--	----	--	9	--	8	12	--	60[d]
	35	21.04							
Molds[a]	--	----	--	8	--	6	12	--	22
Bacteria[b]	--	----	--	1155	--	2381	1768	--	1500
				1500[d]		1900[d]	1486[d]		
Yeasts and spores[c]	--	----	--	18	--	6	8	--	67[d]

[a] Expressed as per cent of microscopic fields showing molds.
[b] Expressed as million bacteria per cc.

4.—Continued.

ANALYST									AVERAGE
5A	6	8	10	12	13	14	14A	15	
SERIES 5.									
16[d]	24[d]	12	--	12	18 16[d]	26	22	12	17
110[d] 42[d]	78[d]	92	--	67	72 108[d] 120[d]	84	64	98	81
14[d]	24[d]	4	--	5	4 4[d]	4	5	12	6
--	18[d]	18	--	4	18	6	8	6	13
--	480[d]	266	--	233	400	281	248	252	279
--	600[d]	28	--	8	4	10	14	4	10
SERIES 6.									
--	10[d]	--	--	--	22	6	8	--	12
--	240[d]	--	--	--	720 960[d]	500	524	--	598
--	175[d]	--	--	--	2	8	12	--	12
30	12[d]	--	--	--	16	16	18	8	20
288[d]	698[d]	--	--	--	720	580	613	716	714
600[d]	44[d]	--	--	--	4	8	13	6	11
SERIES 7.									
--	20[d]	16	--	--	14	10	10	8[d]	16
--	240[d]	372	--	--	480	312[d]	295[d]	324[d]	416
--	14[d]	2	--	--	1	17	16	5[d]	9
--	18	--	--	--	16	8	8	--	12
--	110[d]	--	--	--	720	700	672	--	701
--	180[d]	--	--	--	2	15	19	--	13
--	--	--	--	--	16	12	10	--	12
--	--	--	--	--	2000[d]	1125	1636	--	1407
--	--	--	--	--	4	19	16	--	13
--	12	--	--	--	10	12	14	--	14
--	750[d]	--	--	--	1800	2097	2092	--	1747
--	200[d]	--	--	--	2	8	72[d]	--	7
--	30[d]	--	--	--	10	0[d]	0[d]	--	12
--	760[d]	--	--	--	2400	2731 2771[d]	2477 3033[d]	--	2130
--	480[d]	--	--	--	4	8	8	--	9

[c] Expressed as number of yeasts and spores per $\frac{1}{60}$ cmm.
[d] Not included in average.

TABLE

DETERMINATION	SAMPLE NUMBER	SOLIDS	ANALYST						
			1	1A	2	3	3A	4	5
			SERIES 8.						
	37	*per cent* 4.88							
Molds[a]	--	----	--	18	--	16	12	--	--
Bacteria[b]	--	----	--	1025	--	979	714	--	--
Yeasts and spores[c]	--	----	--	12	--	6	697[d] 15	--	--
	38	11.70							
Molds[a]	--	----	--	10	--	16	13	--	--
Bacteria[b]	--	----	--	1180 900[d]	--	1748	1483	--	--
Yeasts and spores[c]	--	----	--	12	--	8	12	--	--
	39	20.10							
Molds[a]	--	----	--	14	--	20	20	--	--
Bacteria[b]	--	----	--	1721 1450[d]	--	2477	2160	--	--
Yeasts and spores[c]	--	----	--	12	--	6	12	--	--
	40	28.80							
Molds[a]	--	----	--	14	--	8	15	--	--
Bacteria[b]	--	----	--	2095 1750[d]	--	2592	3000	--	--
Yeasts and spores[c]	--	----	--	15	--	12	18	--	--

[a] Expressed as per cent of microscopic fields showing molds.
[b] Expressed as million bacteria per cc.

TABLE

Bacterial count of pulp samples in Table 4

(Expressed as million

SAMPLE NUMBER	ANALYST							
	1	1A	2	3	3A	4	5	5A
	SERIES 1.							
9	32	30	34	20	39	22	12	5
10	--	6	--	27	28	20	9	--
11	--	11	--	19	18	16	--	16
12	21	17	21	15	12	13	7	9
	SERIES 2.							
14	8	7	7	12	18	30	13	8
15	--	5	--	5	13	--	12	--
16	10	10	--	19	15	8	12	10

4.—Concluded.

ANALYST									AVERAGE
5A	6	8	10	12	13	14	14A	15	
SERIES 8.									
6	20	--	--	--	12	8	20	--	14
1000	230[d]	--	--	--	875	880	1070	--	935
40	450[d]	--	--	--	3	18	18	--	16
11	17	8	--	--	36 16[d]	8	6	--	15
1100	480[d]	1600	--	--	960	1134	1478	--	1298
32	80[d]	18	--	--	3	20	24	--	16
6	15	--	--	--	14	10	16	--	14
1000[d]	350[d]	--	--	--	2400	2328	1931	--	2170
44	225[d]	--	--	--	4	16	12	--	15
--	24	10	--	--	20	10	6	--	13
--	800[d]	4200	--	--	3000	3888	2688	--	3066
--	160[d]	12	--	--	6	320[d]	116[d]	--	13

[c] Expressed as number of yeasts and spores per $\frac{1}{50}$ cmm.
[d] Not included in average.

5.

calculated to pulp of 8.37 per cent solids.

bacteria per cc.)

ANALYST							AVERAGE
8	10	12	13	14	14A	15	
SERIES 1.							
35	20	17	25	8	12	--	22
14	--	--	16	4	7	--	14
13	--	--	11	11	7	--	14
10	8	11	15	--	--	--	13
SERIES 2.							
13	15	8	23	8	7	17	13
18	--	8	10	4	3	23	10
12	--	3	18	2	7	13	11

TABLE

SAMPLE NUMBER	ANALYST							
	1	1A	2	3	3A	4	5	5A
				SERIES 3.				
21	12	8	21	23	23	20	25	37
41	--	14	--	19	10	23	--	16
42	--	7	--	16	11	16	7	--
25	--	8	--	18	14	9	16	11
				SERIES 4.				
47	--	21	--	21	26	37	--	8
22	9	6	16	13	11	16	25	22
45	--	11	--	14	14	--	9	--
46	--	11	--	21	25	12	16	16
				SERIES 5.				
26	--	97	--	132	140	--	157	--
29	--	110	--	280	174	--	145	--
				SERIES 6.				
31	--	215	--	352	210	--	408	---
27	--	245	--	304	267	--	---	326
				SERIES 7.				
28	--	597	--	755	694	--	704	--
32	--	699	--	710	696	--	1096[a]	--
33	--	---	--	985	964	--	594	--
34	--	554	--	872	798	--	704	--
35	--	657	--	946	702	--	596	--
				SERIES 8.				
37	--	1758	--	1679	1223	--	--	1712
38	--	845	--	1252	1061	--	--	787
39	--	716	--	1030	899	--	--	417[a]
40	--	608	--	754	872	--	--	---

[a] Not included in average.

5.—Concluded.

ANALYST							AVERAGE
8	10	12	13	14	14A	15	
Series 3.							
32	20	17	25	7	8	--	21
--	--	--	16	5	7	--	14
28	--	12	8	3	4	--	12
17	13	15	15	4	4	--	12
Series 4.							
40	23	--	37	18	38	--	27
32	37	--	16	11	5	--	17
35	15	--	12	2	2	--	13
9	14	--	17	--	--	--	16
Series 5.							
144	--	105	113	130	101	154	127
171	--	150	258	181	160	162	180
Series 6.							
--	--	--	350	244	255	--	292
--	--	--	267	215	265	--	269
Series 7.							
--	--	--	802	522[a]	494[a]	--	712
--	--	--	716	697	668	--	697
--	--	--	1190[a]	669	974	--	837
--	--	--	844	984	982	--	819
--	--	--	954	1087	955	--	846
Series 8.							
--	--	--	1499	1504	1835	--	1601
--	--	--	686	812	1040	--	954
--	--	--	1000	969	804	--	904
--	--	--	872	1129	781	--	890

[a] Not included in average.

TABLE

Microscopic count of trimming-stock pulp prepared from raw

DETERMINATION	SAMPLE NUMBER	ROT IN TOMATOES	ANALYST					
			1	1A	3	3A	4	5
		per cent						
	8	1.8						
Molds[a]	--	----	51	61	76	70	46	--
Bacteria[b]	--	----	19	14	24	26	20	--
Yeasts and spores[c]	--	----	16	10	24	28	25	--
	13	Less than 1.00						
Molds[a]	--	----	39	48	52	48	32[d]	46
Bacteria[b]	--	----	8	5	12	8	8	19
Yeasts and spores[c]	--	----	12	5	12	12[d] 10	16	9
	19A	2.88[e]						
Molds[a]	--	----	89	86	80	72	--	82
Bacteria[b]	--	----	36	38	56	41	--	67
Yeasts and spores[c]	--	----	23	15	86[d]	46[d]	--	22
	19B	2.88[e]						
Molds[a]	--	----	52	52	50	52	--	--
Bacteria[b]	--	----	26	38	19	16	--	--
Yeasts and spores[c]	--	----	18	11	28	22	--	--
	19C	2.88[e]						
Molds[a]	--	----	50	46	59	54	--	72[d]
Bacteria[b]	--	----	33	41	31	22	--	12
Yeasts and spores[c]	--	----	14	17	26	20	--	36
	49	2.00						
Molds[a]	--	----	70	80	61	74	47[d]	--
Bacteria[b]	--	----	29	42	31	28	36	--
Yeasts and spores[c]	--	----	20	18	21	28	27	--
	50	1.97						
Molds[a]	--	----	53	68	69	58	44	--
Bacteria[b]	--	----	15	14	29	13	35	--
Yeasts and spores[c]	--	----	16	19	28	18	18	--
	51	0.30						
Molds[a]	--	----	36	44	32	44	26	54
Bacteria[b]	--	----	29	22	29	14	36	5[d]
Yeasts and spores[c]	--	----	13	7	18	12	8	16
	9	1.00						
Molds[a]	--	----	20	34	24	25	21	32
Bacteria[b]	--	----	19	18	12	23	13	7
Yeasts and spores[c]	--	----	7	9	2	12	9	7

[a] Expressed as per cent of microscopic fields showing mold.
[b] Expressed as million bacteria per cc.
[c] Expressed as number of yeasts and spores per $\frac{1}{60}$ cmm.

6.

product containing known amounts of rotting material.

ANALYST									AVERAGE
5A	6	8	10	12	13	14	14A	15	
56	58[d]	44	53	24[d]	58	70	64	44	58
12	28[d]	18	22	26	12	4	11	26	18
					50[d]				
17	600[d]	18	9	--	12	12	16	14	17
--	78[d]	38	47	28[d]	44	52	64[d]	56	47
					30[d]			68[d]	
--	18[d]	6	5	4	5	5	3	10	8
--	49[d]	9	5	22	13	8	10	8	11
--	--	--	78	92	--	--	--	--	83
--	--	--	29	36	--	--	--	--	43
--	--	--	13	20	--	--	--	--	19
52	--	--	53	46	--	--	--	--	51
14	--	--	24	20	--	--	--	--	22
32	--	--	14	18	--	--	--	--	20
--	--	--	65	50	--	--	--	--	54
--	--	--	31	30	--	--	--	--	29
--	--	--	16	18	--	--	--	--	21
82	98[d]	46[d]	84	56	86	74	70	64	73
80[d]					74[d]			94[d]	
28	32[d]	19	16	13	28	6[d]	5[d]	40	28
24	54[d]	14	18	13	30	35[d]	42[d]	11	20
69	85[d]	42	79	28[d]	56	32[d]	--	52	59
5[d]	35[d]	14	21	10	40[d]	22	--	34	21
					48[d]				
24	39[d]	16	16	12	16	9	--	12	17
--	70[d]	38	44	16[d]	44	36	--	28	39
--	44[d]	26	18	8[d]	125[d]	7	--	34	24
--	64[d]	8	9	4	10	9	--	14	11
28	38[d]	24	24	28	30	30	28	--	27
3	9[d]	21	12	10	15	5	7	--	13
8	22[d]	5	5	--	4	8	6	--	7

[d] Not included in average.

[e] This figure is the average per cent of rot during a period when a number of batches of pulp were run. Therefore it does not accurately represent the amount of rot in the tomatoes for any individual batch.

TABLE

Influence of delay in manufacture

DETERMINATION	SAMPLE NUMBER	STORAGE	ANALYST			
			1A	3	3A	4
		hours				
	26	2				
Molds[a]	--	--	6	20	22	18
Bacteria[b]	--	--	62	84	89	210[d]
				79[d]	91[d]	
Yeasts and spores[c]	--	--	1	1	4	5
	28	8				
Molds[a]	--	--	10	22	20	3[d]
Bacteria[b]	--	--	357	451	415	990[d]
			338[d]			
Yeasts and spores[c]	--	--	2	4	6	4[d]
	36	12				
Molds[a]	--	--	10	22	16	3
Bacteria[b]	--	--	396	874	520	990
			412[d]		842[d]	
Yeasts and spores[c]	--	--	2	10	15	4

[a] Expressed as number of microscopic fields showing mold.
[b] Expressed as million bacteria per cc.

7.

on microscopic count.

ANALYST									AVERAGE
5	5A	6	8	12	13	14	14A	15	
20	16[d]	24[d]	12	12	18	26	22	12	17
100	110[d]	78[d]	92	67	72	84	64	98	81
36[d]	42[d]				108[d]				
20	14[d]	24[d]	4	5	4	4	5	12	6
28	--	20[d]	16	--	14	10	10	8[d]	16
420	--	240[d]	372	--	480	312[d]	295[d]	324[d]	416
						536[d]	320[d]		
15	--	14[d]	2	--	1	17	16	5[d]	9
6	--	20[d]	6	--	14	18	24	8	13
420	--	240[d]	509	--	480	310	487	324	531
15	--	14[d]	14	--	7	14	10	5	10

[c] Expressed as number of yeasts and spores per $\frac{1}{50}$ cmm.
[d] Not included in average.

TABLE

Influence of finishing on the

DETERMINATION	SAMPLE NUMBER	DESCRIPTION	ANALYST				
			1	1A	2	3	3A
SERIES 1.							
	23	Unfinished					
Molds[a]	--	----	60	40 58[d]	42	49	46
Bacteria[b]	--	----	19	20 17[d]	20	19	22
Yeasts and spores[c]	--	----	12	7	8	20	26
	48	Finished					
Molds[a]	--	----	38	48	--	46	53
Bacteria[b]	--	----	22	28	--	29	16
Yeasts and spores[c]	--	----	13	8	--	20	18
SERIES 2.							
	17	Unfinished					
Molds[a]	--	----	28	20	--	22	32
Bacteria[b]	--	----	10	14	--	29	26
Yeasts and spores[c]	--	----	9	15	--	34	28
	18	Finished					
Molds[a]	--	----	28	36	--	26	30
Bacteria[b]	--	----	13	18	--	24	29
Yeasts and spores[c]	--	----	18	11	--	14	24
SERIES 3.							
	43	Unfinished					
Molds[a]	--	----	28	28	--	27 41[d]	31
Bacteria[b]	--	----	10	16	--	34	23
Yeasts and spores[c]	--	----	20	5	--	22	18
	44	Finished					
Molds[a]	--	----	28	28	--	29	28
Bacteria[b]	--	----	15	15	--	38	23
Yeasts and spores[c]	--	----	11	9	--	21	28

[a] Expressed as number of microscopic fields showing mold.
[b] Expressed as million bacteria per cc.

8.

microscopic count of tomato pulp.

ANALYST											AVERAGE
4	5	5A	6	8	10	12	13	14	14A	15	
SERIES 1.											
16	42	39	86[d]	--	50	4[d]	42 40[d]	--	--	54	43
26	14	15	48[d]	--	13	14	18	--	--	36	20
--	59[d]	63[d]					60[d]				
							17[d]				
13	32	32	66[d]	--	6	10	20 14[d]	--	--	5	18
31	54	48	80[d]	20	--	20	40	--	--	48 66[d]	43
24	23	36	33[d]	21	--	24	28	--	--	36 39[d]	27
19	14	20	38[d]	14	--	5	14	--	--	9	14
SERIES 2.											
8	14 32[d]	--	40[d]	8	34	12	24	12	24	28	22
17	17 17[d]	--	48[d]	14	15	10	28 60[d]	4	11	26	17
9	22 25[d]	--	114[d]	16	12	10	16	24	18	8	17
11	26	--	35[d]	10	37	14	30	10	24	44	25
16	16	--	29[d]	22	14	38	24 50[d]	12	16	38	22
30	23	--	30[d]	22	8	2	6	30	24	10	19
SERIES 3.											
24	--	20	26[d]	14	32	4	22	16	--	34	23
25	--	6 32[d]	48[d]	35	11	11	22	8	--	22	19
28	--	23	46[d]	13	5	10	10	15	--	18	16
19	--	20	8[d]	20	32	8	22 32[d]	28	--	28	24
19	--	20	34[d]	12	4	13	30 42[d]	4	--	24	23
16	--	16	40[d]	10	11	6	8 12[d]	16	--	18	14

[c] Expressed as number of yeasts and spores per $\frac{1}{60}$ cmm.
[d] Not included in average.

REPORT ON COCOA AND COCOA PRODUCTS.

By EUGENE BLOOMBERG[1] (Bureau of Chemistry, Food and Drug Inspection Station, Buffalo, N. Y.), *Associate Referee.*

The name "Cocoa and Cocoa Products" is rather inaccurate. Cocoa is merely one of the products made from the bean of the *Theobroma cacao.* Neither chocolate nor cacao butter is a cocoa product. All of these can properly be classified as "Cacao Products". This nomenclature has been adopted by the Bureau of Chemistry in the information cards and by the Committee on Editing Methods of Analysis and should be adopted by the Association of Official Agricultural Chemists.

MILK CHOCOLATE.

At the 1914 meeting it was recommended that the associate referee on cocoa products for the year 1915 make a study of the manufacture of milk chocolate with a view to finding out whether different methods of manufacture might render the casein insoluble in the reagents used for its extraction in the examination of milk chocolate. No work was done in 1915 on this recommendation. At about that time the present associate referee had occasion to do some work on this subject. It was felt in some quarters that continued heating might have the effect of rendering the casein in milk chocolate insoluble in the 1 per cent sodium oxalate solution which was used for its extraction. To ascertain whether or not this was true, milk chocolate of known milk content, milk powder and commercial casein were heated at a temperature of 60°C. (which is the highest temperature to which milk chocolate is heated in the process of manufacture), for a period of 192 consecutive hours, samples being taken from each every 24 hours. The samples taken from each product at each period were analyzed and the amount of casein found in each product did not vary over the 192-hour period. Evidently, heating these products did not render the casein contained therein insoluble in 1 per cent sodium oxalate solution.

Samples were then collected by the associate referee in person from factories to ascertain whether casein was rendered insoluble by the various methods of manufacture. There are three principal methods in the manufacture of milk chocolate, the differences being in the way the milk is added: First, using fresh milk; second, using condensed milk; third, using milk powder. Samples were taken at various stages of manufacture from each concern and analyzed to ascertain whether by any steps in the manufacture casein might be rendered insoluble in the sodium oxalate solution.

---

[1] Present address, P. O. Box 54, Station E, Cleveland, Ohio.

TABLE 1.

Determinations of casein in milk chocolate at various stages of manufacture.

METHOD OF MANUFACTURE	STAGE OF MANUFACTURE	CASEIN FOUND	CASEIN THEORETICAL
		per cent	*per cent*
Sample 1:			
From fresh milk	Mixed	4.24	4.14
From fresh milk	Rolled	4.14	4.14
From fresh milk	Conched	4.29	4.14
Sample 2:			
From fresh milk	Mixed	4.24	4.32
From fresh milk	Rolled	4.28	4.32
From fresh milk	Conched	4.24	4.32
From condensed milk	Mixed	1.22	1.12
From condensed milk	Finished	1.18	1.12
From milk powder	Mixed	3.13	3.26
From milk powder	Finished	3.10	3.26

The results obtained in this investigation would appear to show conclusively that the process of manufacture does not render casein insoluble in the reagent used.

During the course of this investigation some trouble was experienced in obtaining theoretical results for casein when analyzed by the Baier and Neumann method[1], which was provisionally adopted by the Association of Official Agricultural Chemists. It seemed that there were two operations in this method whereby errors might enter. In the first place, although the method calls for a thorough rubbing up of the defatted chocolate with the sodium oxalate, this material has a tendency to settle out, and it is possible that in some cases not all of the material present is acted upon by the solvent. This would have the effect of giving results which would be too low. On the other hand, there is a possibility that on the precipitation of the casein other bodies are carried down which might with difficulty be removed from the precipitate by washing, especially as this precipitate is rather sticky. Minor objections are that the heating in a 250 cc. flask had to be cautiously done to avoid foaming over and that the filtration of the sodium oxalate solution was very slow.

To ascertain whether the defatting operation was necessary, casein was determined in samples both with and without previous defatting, and it was found that no necessity existed for defatting the sample; in fact, if anything, the heat dissolved the fat from the milk chocolate and left the chocolate material in a very finely divided condition, so that the action of the sodium oxalate was accelerated.

In order to obviate the necessity of washing the acetic acid precipitate,

[1] *Z. Nahr. Genussm.*, 1909, **18**: 17.

the following modification of the Baier and Neumann method was worked out by the associate referee:

Transfer 10 grams of grated milk chocolate to a 500 cc. Erlenmeyer flask. Add 250 cc. of 1% sodium oxalate solution, heat to boiling and boil for about 2 minutes. Allow to cool, add 5 grams of magnesium carbonate and filter. Determine nitrogen in 50 cc. of the filtrate, corresponding to 2 grams of the original chocolate. Pipette 100 cc. of the filtrate into a 200 cc. flask, make nearly to volume, then add 2 cc. of glacial acetic acid. Make to volume, shake, allow to stand for some time, so that the precipitate may settle somewhat, then filter. Determine nitrogen on 100 cc. of the filtrate, which also corresponds to 2 grams of chocolate. The difference in the amounts of nitrogen is the nitrogen which is present as casein. This, multiplied by 6.38, gives casein present in 2 grams of milk chocolate.

TABLE 2.

Casein determinations.

(Analyst, Eugene Bloomberg.)

METHOD OF MANUFACTURE	THEORETICAL AMOUNT	BAIER AND NEUMANN METHOD DEFATTED	BAIER AND NEUMANN METHOD WITHOUT DEFATTING	ASSOCIATE REFEREE'S MODIFICATION
	per cent	*per cent*	*per cent*	*per cent*
Made from condensed milk	1.12	----	0.80	1.16
Made from condensed milk	2.31	1.76	1.52	2.18
	----	----	----	2.18
	----	----	----	2.32
	----	----	----	2.36
Made from condensed milk	1.09	----	0.57	1.11
	----	----	----	1.18
Made from whole milk	4.14	3.80	3.92	4.14
	----	3.94	4.12	4.24
	----	4.18	4.24	4.29
	----	4.31	4.42	----
Made from whole milk	4.32	4.58	4.12	4.20
	----	4.90	4.28	4.24
	----	----	4.38	4.24
Made from milk powder	3.50	----	----	3.17
	----	----	----	3.26
	----	----	----	3.34
	----	----	----	3.35
Made from milk powder	3.26	----	----	3.13
	----	----	----	3.13
	----	----	----	3.17
Made from milk powder	3.58	----	----	3.53
	----	----	----	3.57
	----	----	----	3.70
Made from milk powder	4.48	----	----	4.59
	----	----	----	4.59
Made from milk powder	3.50	----	----	3.53
	----	----	----	3.61

A large number of samples of known milk content were examined by this method and also by the Baier and Neumann method, with results as given in Table 2. These samples were all made under the direction of the associate referee, the milk used being analyzed and the casein calculated as 80 per cent of the milk protein.

It will be noted that, where there is a considerable amount of casein present, the Baier and Neumann method, either with or without defatting, gives results very close to the theoretical. However, where there is but a small amount of casein present, this method tends to give results which are considerably low. The proposed method, however, gives results which are very close to the theoretical, irrespective of the amount of casein present.

COOPERATIVE WORK.

One sample of milk chocolate was sent to eleven collaborators and reports were received from nine. The following directions were sent out:

Fat.—Determine fat on a 2-gram sample, using anhydrous ethyl ether, extracting in a Knorr or similar condenser for 4 hours. Evaporate off the ether, weigh the ether extract and repeat the extraction for another 4 hours, reporting results obtained at the end of 4 hours; also results obtained at the end of 8 hours. Also report if there seems to be any theobromin in the residue of either extract.

Casein.—Determine casein by the method given in the 1912 Proceedings[1]. It is unnecessary to add uranium acetate in the precipitation and in washing of the precipitate.

Also determine casein by the following method:

(It is unnecessary to defat the chocolate.) Weigh 10 grams of chocolate into a 500 cc. Erlenmeyer flask and add 250 cc. of 1% sodium oxalate solution. Heat to boiling and boil gently for a few minutes; then cool, add 5 grams of magnesium carbonate and filter. Determine nitrogen on 50 cc. of this filtrate, corresponding to 2 grams of the original sample. Pipette 100 cc. of the filtrate into a 200 cc. volumetric flask and make almost to the mark with water. Then precipitate the casein by the addition of 2 cc. of glacial acetic acid. Make to volume, shake, filter, and determine nitrogen on 100 cc. of the filtrate. The difference in the two nitrogen determinations gives nitrogen derived from the casein, which, multiplied by 6.38, will give the amount of casein present in 2 grams of the sample.

Report which method you consider the better from the standpoint of time and convenience.

Sucrose and lactose.—Determine sucrose and lactose by the polariscopic method[2] except that the present formulæ[3] are used in place of those there given.

Determine lactose by copper by heating on a water bath 10 grams of the chocolate in a 250 cc. volumetric flask with approximately 200 cc. of water, shake occasionally so that all sugar is dissolved. Clarify with lead subacetate, make to mark, filter, remove the lead and determine lactose on 50 cc. aliquot. Report lactose as anhydrous lactose.

---

[1] U. S. Bur. Chem. Bull. 162: 130.
[2] *Ibid.*, 137: 98.
[3] *Assoc. Official Agr. Chemists, Methods*, 1916, 329.

TABLE 3.

Results reported by collaborators on milk chocolate.

ANALYST	FAT	FAT	SUCROSE	LACTOSE		CASEIN	
	4-hour extraction	8-hour extraction	Polariscopic determination	Polariscopic determination	Copper method	Baier and Neumann method	Proposed method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
J. Callaway, jr., U. S. Food and Drug Inspection Station, U. S. Custom House, Savannah, Ga.	33.06	33.06	39.33	8.19	7.68	3.52	3.30
W. C. Taber, Bureau of Chemistry, Washington, D. C.	32.64	32.80	40.56	6.89	7.40	3.74	3.85
W. L. Dubois, Hershey, Pa.	32.82	33.12	40.00	6.56	----	3.50	2.08[a]
C. L. Black, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, Philadelphia, Pa.	32.84 32.80 ----	32.84 32.84 ----	39.92 ---- ----	6.90 ---- ----	7.14 ---- ----	4.15 4.02 3.96[b]	4.03 ---- ----
Leonard Feldstein, U. S Food and Drug Inspection Station, Tabor Opera House Building, Denver, Colo.	32.80 32.70	32.92 32.81	38.00[a] ----	5.90[a] ----	7.00 ----	---- ----	3.54 3.34
A. G. Woodman, Massachusetts Institute of Technology, Boston, Mass.	32.93	33.08	40.05	6.41	----	3.57	----
C. E. Warriner, U. S. Food and Drug Inspection Station, Territorial Board of Health, Honolulu, Hawaii.	33.07	33.21	----	----	----	3.50	3.04[a]
A. S. Wells, Dairy and Food Commission, Portland, Ore.	33.03 33.01	33.56 33.52	43.81 ----	8.18 ----	7.81 7.91	3.56[b] ----	3.74 ----
F. T. Anderson, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.	31.56	31.56	40.33	6.60	7.39	3.80	3.76
Eugene Bloomberg, U. S. Food and Drug Inspection Station, Federal Building, Buffalo, N. Y.	32.75 32.78	32.85 32.88	40.01 ----	6.75 ----	7.59 ----	---- ----	4.16 ----
Maximum	33.07	33.56	43.81	8.19	7.91	4.15	4.16
Minimum	31.56	31.56	39.33	6.41	7.00	3.50	3.30
Average	32.77	32.93	40.50	7.06	7.49	3.73	3.72
Theoretical	----	----	40.00	7.00	7.00	4.14	4.14

[a] Omitted from averages.
[b] Not defatted for casein determination.

Messrs. Callaway, Feldstein, Warriner and Anderson report theobromin present in both the 4- and 8-hour fat extractions; Messrs. Taber, Dubois, Woodman and Bloomberg report theobromin present in the second extraction only; Mr. Black reports no theobromin found.

Messrs. Callaway, Warriner and Wells prefer the proposed method for casein determination; Messrs. Dubois and Black prefer the first. The others indicated no preference.

DISCUSSION.

Several of the collaborators called attention to the fact that while the instructions called for lactose by copper to be reported as anhydrous, the normal way in which lactose occurs, and the way it is calculated by the formula from the polariscopic readings, is with 1 molecule of water. This is correct, and lactose by copper should be reported as monohydrated. Calculating by this table, Mr. Taber found 6.89 per cent of lactose (monohydrated) present. Mr. Taber pointed out, however, that the presence of sucrose gives results for lactose by copper which are high, and a table should be used for this determination which takes into account the sucrose.

The formula sent out for the polariscopic determination of sucrose and lactose was worked out by Messrs. Seeker, Shanley and Lourie of the U. S. Food and Drug Inspection Station of the Bureau of Chemistry, New York, N. Y. The formula as adopted by the association in 1910 calculates the amounts of sugars present and then calculates the increase of volume due to these sugars, the percentage of sugars then being corrected to account for this increased volume. This, while near enough for ordinary purposes, is not exactly correct. The formula sent out this year calculates the increase of volume directly from the polarization and is theoretically correct.

It seems to be unnecessary to dry over sulphuric acid before extracting fat with ether. Mr. Callaway obtained 33.06 per cent of fat without drying, and 32.96 per cent after drying. Your referee obtained 32.78 and 32.75 per cent without drying, and 32.77 and 32.78 per cent after drying. The results obtained on the fat extraction seem to show conclusively that a 4-hour extraction, using anhydrous ethyl ether, removes all the fat present in a product of this nature. Long extractions are not necessary on cacao products for the reason that in their manufacture they are ground very finely and for this reason the fat is easily extracted. Moreover, it appears that a longer continued extraction will extract a portion of the theobromin.

There is a difference of opinion as to which casein method is the shorter and more easily carried out, although the results obtained are about the same by either method. The associate referee has made

several hundred determinations and prefers the new method, but there is no doubt that Mr. Black's objection is well taken, that there is considerable frothing of the sodium oxalate solution when treated with sulphuric acid, due to the evolution of carbon monoxid. Several other solvents were tried, but in no case did they give as good results as the sodium oxalate.

CACAO BUTTER SUBSTITUTES.

The detection of cacao butter substitutes in cacao products offers some difficulty, especially if these substitutes are present in small amounts. The general method of procedure is to determine the constants on the extracted fat and to depend upon these determinations for the detection and identification of the cacao butter substitute used. If a substitute is present in amounts of from 5 to 10 per cent, it is with difficulty detected; in fact, some of the substitutes, especially tallow and hydrogenated cottonseed oil, have constants so near those of cacao butter that it is practically impossible to detect their presence by this procedure.

It was desired to find a short and more exact method for the detection of the presence of cacao butter substitutes. Such a method has been found in the critical temperature of dissolution of the fat in glacial acetic acid. For a given strength of glacial acetic acid the critical temperature of dissolution of a cacao butter is constant within 1°. This test is practically the Valenta test[1]. It is made by adding 5 cc. of the melted filtered fat to an equal volume of glacial acetic acid in a test tube, the whole being heated, with constant stirring, until the fat goes into solution. The solution is then allowed to cool (stirring with a thermometer) and the temperature at which turbidity appears is the critical temperature of dissolution. The critical temperature of dissolution of any fat varies with the strength of acetic acid used. Inasmuch as slight differences in the strength of the acetic acid make considerable difference in the critical temperature of dissolution, it was thought advisable in this determination to standardize the acetic acid each time it was used against an authentic sample of cacao butter, rather than attempt to use an acetic acid of definite strength. Since this is the case, it is not the critical temperature of dissolution found which is indicative of the purity or adulteration of the sample, but rather the variation of the sample from an authentic sample of cacao butter.

Practically all substitutes give a critical temperature of dissolution considerably below that of true cacao butter. Using an acetic acid with which pure cacao butter gave a critical temperature of dissolution of 96°C., shell butter gave 71°C., coconut and palm kernel products

[1] *J. Soc. Chem. Ind.*, 1884, 3: 643.

16°C., hydrogenated cottonseed oil 104°C., tallow 94°C., corn oil 20°C., cottonseed oil 46°C., olive oil 63°C., peanut oil 52°C., sesame oil 40°C. Mixtures of any of these products with pure cacao butter changed the critical temperature of dissolution by an amount approximately proportional to the amount of substitute used.

The only substitutes in use which have a critical temperature of dissolution equal to or greater than cacao butter are hydrogenated oils and tallow. These adulterants may be detected by adding 5 cc. of the melted fat to 5 cc. of a mixture of equal parts of acetone and carbon tetrachlorid and allowing the mixture to stand in ice-water. In the presence of either hydrogenated oil or tallow a flocculent precipitate will be formed in from 5 to 30 minutes, depending upon the amount of adulterant present. This test is simpler, much more exact, and will detect smaller additions of tallow than will Björklund's ether test[1].

These two tests may be easily and quickly made and give an almost certain indication as to the presence or absence of cacao butter substitutes as well as some indication of the kind of substitute used. To ascertain the exact identity of the substitute, it is necessary to determine some of the ordinary constants. If, however, the critical temperature of dissolution is approximately that of cacao butter, and neither hydrogenated oil nor tallow is found, it is almost certain that the product under examination is a pure cacao butter.

COLLABORATIVE WORK.

The following samples were sent to collaborators:

Sample 1.—A mixture of 80 per cent cacao butter and 20 per cent coconut oil stearin.

Sample 2.—A mixture of 80 per cent cacao butter and 20 per cent cottonseed oil.

Sample 3.—A mixture of 80 per cent cacao butter and 20 per cent coconut oil stearin. (This sample is practically the same as No. 1, except that the coconut oil stearin is put out by a different manufacturer under a different name.)

Sample 4.—A mixture of 80 per cent cacao butter, 10 per cent coconut oil and 10 per cent corn oil.

Sample 5.—A mixture of 80 per cent cacao butter, 15 per cent coconut oil and 5 per cent tallow.

Sample 6.—A mixture of 95 per cent cacao butter and 5 per cent coconut oil.

Sample 7.—Pure cacao butter.

There was also forwarded a sample of cacao butter which was to be used as a standard.

INSTRUCTIONS TO COLLABORATORS.

Make the critical temperature of dissolution determination and report results obtained on each sample, also those obtained on the authentic sample of cacao butter, using the same acetic acid on all tests. Make a test for tallow and hydrogenated oil, using 5 cc. of the melted fat and 5 cc. of acetone. Heat if necessary to dissolve, and

[1] *Z. anal. Chem.*, 1804, **3**: 233.

allow the mixture to stand in cold water overnight, running a blank with pure cacao butter at the same time. A white flocculent precipitate indicates the presence of either tallow or hydrogenated oil. Should either of these tests give results which would indicate the presence of a foreign fat, it is requested that other determinations, such as the saponification number and iodin number, be made in order to determine, if possible, the kind and percentage of adulterant in each sample.

TABLE 4.

Collaborative results on cacao butter substitutes.

ANALYST	CRITICAL TEMPERATURE OF DISSOLUTION	DIFFERENCE FROM CACAO BUTTER	ACETONE TEST	SAPONIFICATION NUMBER	IODIN NUMBER	CONCLUSIONS
			SAMPLE 1.			
	°C.	°C.				
1	71.0	−17.0	negative	203.4	28.4	20 per cent coconut or palm kernel stearin present.
2	83.5	−13.0	slight ppt.	206.3	29.6	20 per cent coconut or palm kernel stearin present.
	----	------	--------	----	29.4	
3	81.5	−16.5	negative	204.2	30.5	20 per cent coconut or palm kernel stearin present.
4	95.5	−11.5	negative	205.3	29.2	Adulterant present.
	----	------	--------	206.3	29.3	
5	75.5	−17.0	negative	205.5	29.2	
			SAMPLE 2.			
1	75.0	−13.0	negative	194.2	47.3	20 per cent corn or palm oil.
2	85.0	−11.5	slight ppt.	195.3	50.2	Largely shell butter.
3	87.0	−11.0	negative	194.8	51.8	20 per cent cottonseed oil present. (Halphen test positive.)
4	100.25	− 6.75	negative	198.2	49.5	Cottonseed oil present. (Halphen test positive.)
	------	------	--------	199.0	49.4	
5	81.5	−11.0	negative	198.2	40.9	
			SAMPLE 3.			
1	70.5	−17.5	negative	204.4	30.0	20 per cent palm or coconut stearin.
2	79.0	−17.5	negative	205.3	29.1	20-25 per cent coconut or palm kernel oil.
	----	------	--------	207.0	29.4	
3	80.0	−18.0	negative	205.5	30.3	20 per cent coconut olein.
4	94.0	−13.0	negative	209.0	29.4	Adulterant present.
	----	------	--------	208.4	29.4	
5	82.0	−10.5	slight ppt.	203.9	29.5	

TABLE 4.—Continued.

ANALYST	CRITICAL TEMPERATURE OF DISSOLUTION	DIFFERENCE FROM CACAO BUTTER	ACETONE TEST	SAPONIFICATION NUMBER	IODIN NUMBER	CONCLUSIONS
			SAMPLE 4.			
	°C.	°C.				
1	71.5	−16.5	negative	198.8	41.5	
2	81.0	−15.5	slight ppt.	201.9	40.8	Largely beef tallow.
	----	------	---------	202.2	41.0	
3	81.0	−17.0	negative	200.7	41.0	Adulterant present.
4	96.25	−10.75	negative	201.1	40.5	Adulterant present.
	----	------	--------	200.1	40.3	
5	74.5	−18.0	negative	199.3	40.5	
			SAMPLE 5.			
1	71.5	−16.5	positive	203.6	29.8	20 per cent hydrogenated cottonseed oil.
2	81.5	−15.0	heavy flocculent ppt.	205.9	29.9	Tallow present.
	----	------		206.3	29.9	
3	82.5	−15.5	positive	204.4	30.0	Tallow present.
4	95.0	−12.0	heavy ppt.	203.0	29.5	
	----	------	---------	202.3	29.7	
5	74.0	−18.5	white flocculent ppt.	206.2	29.8	
			SAMPLE 6.			
1	79.0	−9.0	negative	195.9	34.8	Less than 10 per cent foreign fat.
2	91.0	−5.5	slight ppt.	197.9	34.0	5 per cent oleo stearin or palm or coconut product.
3	93.0	−5.0	negative	197.3	34.5	Adulterant present.
4	105.0	−2.0	negative	198.6	33.6	Adulterant present.
	----	-----	--------	197.8	33.9	
5	86.5	−6.0	negative	197.3	33.8	
			SAMPLE 7.			
1	88.0	0.0	negative	192.3	36.0	Pure cacao butter.
2	97.0	+0.5	negative	194.2	36.0	Pure cacao butter.
3	101.0	+3.0	positive	193.7	36.5	Hydrogenated cottonseed oil present.
4	108.0	+1.0	negative	194.5	35.8	Pure cacao butter.
5	92.5	0.0	cloudy	195.2	35.8	

TABLE 4.—Concluded.

ANALYST	CRITICAL TEMPERATURE OF DISSOLUTION	DIFFERENCE FROM CACAO BUTTER	ACETONE TEST	SAPONIFICATION NUMBER	IODIN NUMBER	CONCLUSIONS
			SAMPLE 8, STANDARD CACAO BUTTER.			
	°C.	°C.				
1	88.0	----	negative	----	----	
2	96.5	----	--------	192.8	35.7	
3	98.0	----	negative	----	----	
4	107.0	----	negative	192.7	35.8	
	----	----	--------	192.1	35.7	
5	92.5	----	--------	195.4	----	

Analysts referred to in above table are:

1. W. C. Taber, Bureau of Chemistry, Washington, D. C.
2. W. W. Karnan, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, Boston, Mass.
3. J. Callaway, jr., U. S. Food and Drug Inspection Station, U. S. Custom House, Savannah, Ga.
4. C. L. Black, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, Philadelphia, Pa.
5. L. D. Elliott, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.

DISCUSSION.

On Samples 1 and 3 the low critical temperature of dissolution, the high saponification number and low iodin number are all indicative of the presence of a coconut oil product. On Sample 2 the low critical temperature of dissolution would indicate the presence of an adulterant and the high iodin number would show that this adulterant was one of the fixed oils. The only way in which it could be definitely recognized would be by making the specific tests, as was done by two of the analysts. On Sample 4 the low critical temperature of dissolution indicates the presence of an adulterant. The high saponification number would indicate the presence of some coconut oil product, and the high iodin number would indicate that one of the fixed oils was also present. Inasmuch as there is no specific test for corn oil, it would be practically impossible to tell exactly what oil was there. Analyst No. 2 reported the presence of beef tallow on this sample, basing his conclusions on the saponification number and the iodin number. However, the critical temperature of dissolution would show conclusively that it was not tallow, as would the acetone test. In Sample 5 the acetone test would show conclusively

the presence of either tallow or hydrogenated cottonseed oil. At the same time, the low critical temperature of dissolution would show the presence of some other adulterant, and this, together with the high saponification number, is practically proof positive that this other adulterant is coconut oil. In Sample 6 the low critical temperature of dissolution and the slightly increased saponification number show the presence of a coconut oil.

As several of the analysts suggested, it is essential that in the critical temperature of dissolution exactly 5 cc. of the melted fat and 5 cc. of acetic acid be used. It may be noted that although Samples 1 and 3 are practically identical, still some of the analysts obtained differences in the critical temperature of dissolution. This may be partly explained by the supposition that they were not careful to use exact amounts of fat and acid. The critical temperature of dissolution obtained by the different analysts on the same sample varied considerably. This is due to the fact that the acetic acid used varied in strength, and, as has been pointed out, a slight variation in the strength of the acetic acid makes a considerable variation in the critical temperature of dissolution. This also shows why it is important to standardize the acetic acid used against an authentic sample of cacao butter each time. In every case where an adulterant was present the critical temperature of dissolution was lowered sufficiently to indicate this fact.

Several of the analysts reported that in the determination of the acetone test a part of the cacao butter solidified on standing, thus somewhat obscuring the flocculent precipitate. However, it will be noted that the flocculent precipitate thrown down when tallow is present is so distinctive that no one failed to note its presence in Sample 5. Moreover, in only one case was a positive test found when no adulterant was present. It was desired if possible to obviate this difficulty and to shorten the time for making this test. With this end in view, the action of a great number of solvents was ascertained, and it was found that by using 5 cc. of a mixture of equal parts of acetone and carbon tetrachlorid with 5 cc. of the melted fat and allowing this to stand in ice-water, a flocculent precipitate was obtained, when either tallow or hydrogenated oil was present, in from 5 to 30 minutes, depending upon the percentage of adulterant.

RECOMMENDATIONS.

It is recommended—

(1) That the name of this subject be changed from "Cocoa and Cocoa Products" to "Cacao Products".

(2) That the present[1] formulæ for the polariscopic determination of

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 329.

sucrose and lactose be adopted as provisional, and that sucrose and lactose be determined by the polariscopic method[1], using the present formulæ.

(3) That a 4-hour extraction with anhydrous ethyl ether be adopted as a provisional method for the determination of fat.

(4) That the proposed modification of the Baier and Neumann method be further studied with a view to its adoption as a provisional method.

(5) That the determination of the critical temperature of dissolution be adopted as a provisional method for the examination of cacao butter.

(6) That the associate referee's test for tallow and hydrogenated oils be adopted as provisional.

REPORT ON TEA AND COFFEE.

By H. M. Loomis (National Canners Association, Mills Building, Washington, D. C.), *Associate Referee.*

No collaborative work was undertaken. Some preliminary experimental work was done, however, in the Bureau of Chemistry, H. A. Lepper and A. W. Broomell collaborating on the determination of moisture, sugars and acidity of coffee, and recommendations for modifying the present provisional methods were made to the Committee on Editing Methods of Analysis.

With the assistance of Dr. A. Viehoever of the Bureau of Chemistry, a preliminary study of the possibility of basing a standard for raw coffee on the maximum amount of unsound coffee beans and foreign matter was also made.

The work on the determination of moisture consisted in the comparison of various methods, but in the absence of any absolute determination of this constituent, the results submitted in Tables 1, 2 and 3 are merely comparative. All of the samples were collected direct from coffee-roasting firms.

The work on the moisture content of coffee stored in paper packages in various climates was made primarily to determine whether it would be practicable to set a maximum standard for moisture in roasted coffee in order to prevent the use of excessive water in quenching or coating the coffee. The results in Tables 4 and 5 show the great variations in moisture due to climatic conditions exclusively. As even the most heavily "quenched" or coated coffees seldom contain over 6 per cent of moisture, it is evident that proof of such addition solely by analytical evidence is hardly possible. In this connection the term "quenching" refers to sprinkling coffee with water in the roasting drums, for the purpose of checking the roast, a practice quite common among coffee roasters.

[1] U. S. Bur. Chem. Bull. 137: 98.

"Coated coffee" refers to coffee which has been treated with sugars, white of egg or some other form of glazing material, for the ostensible purpose of preserving its flavor and aroma.

TABLE 1.

Green and roasted coffees, ground and analyzed by A. W. Broomell and H. A. Lepper.

(December 1914, to January 1915.)

DESCRIPTION OF COFFEE	DRIED IN VACUUM AT 98–99°C.		DRIED IN AIR AT 105°C.	
	Loss	Became constant	Loss	Became constant
	per cent	*hours*	*per cent*	*hours*
Brazilian:				
Raw	6.22	9	5.80	9
Plain roast	2.43	9	1.97	5
Roasted, glazed or coated	2.74	9	2.26	5
Rio and Victoria blend:				
Raw	9.45	6	8.96	8
Roasted and quenched	1.78	6	1.83	5
Roasted, not quenched	1.17	6	1.33	7
Roasted and glazed	3.24	6	3.22	6
Rio, type No. 7:				
Raw	5.83	7	5.85	6
Plain roast	3.89	6	3.98	5
Roasted and glazed	5.14	6	5.03	5
Victoria, type No. 7:				
Raw	5.81	6	5.88	5
Plain roast	2.99	7	2.86	6
Roasted and glazed	3.98	7	3.96	7
Rio, type No. 4:				
Raw	5.76	6	5.93	7
Plain roast	3.06	7	3.05	6
Roasted and glazed	3.84	7	3.85	7
Victoria:				
Roasted and glazed	4.98	7	5.01	7

In the determination of reducing sugars in coffee by the copper reduction method, it was found that the filtration of the cuprous oxid was very materially retarded by a flocculent precipitate, which in some cases entirely stopped filtration. This precipitate was found to contain magnesium and iron, probably as hydroxid precipitated by the sodium hydroxid of the Fehling solution. Volumetric methods for the determination of reducing sugars are not applicable because of the deep green color, produced by the alkali, especially with raw coffee, which interferes with the end point. The procedure adopted for this determination was the method for total sugars in foods and feeding stuffs[1], with the addition of 1 gram of powdered ammonium sodium phosphate to the sample,

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 109.

with the 50 per cent alcohol. This reagent, in the presence of alcohol, precipitates enough of the interfering metals to allow easy filtration of the cuprous oxid, but does not entirely eliminate them, so that the weight of the cuprous oxid can not be used, but the amount of copper reduced must be determined volumetrically or electrolytically. It may be added that this alcoholic digestion method is preferable because raw coffee ferments very rapidly in water solution.

Unfortunately, lack of time has made it impossible for H. A. Lepper, who did the work on this method, to submit any figures for reducing sugars obtained by this modified method.

TABLE 2.

Determination of moisture in one type of Brazilian coffee by different methods.

(A. W. Broomell, Analyst.)

DESCRIPTION OF SAMPLE	PERIOD OF HEATING	IN VACUUM AT 70°C.	IN VACUUM AT 97°C.	IN CURRENT OF CARBON DIOXID AT 98°C.	IN WATER OVEN AT 97°C.	IN AIR OVEN AT 105°C.
	hours	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Raw	5	4.14	5.87	4.86	5.35	5.57
Raw	7	4.61	6.07	5.56	5.38	5.65
Raw	9	4.60	6.22	5.76	5.51	5.80
Raw	11	4.67	6.20	5.77	5.57	5.86
Roasted	5	1.52	2.10	1.34	1.85	1.97
Roasted	7	1.76	2.25	1.94	1.82	1.87
Roasted	9	1.69	2.43	2.10	1.74	1.96
Roasted	11	1.75	2.25	2.05	1.76	1.97
Roasted and coated	5	1.75	2.36	1.70	2.19	2.26
Roasted and coated	7	2.08	2.62	2.24	2.17	2.15
Roasted and coated	9	1.90	2.74	2.39	2.04	2.26
Roasted and coated	11	1.95	2.66	2.31	2.05	2.25

TABLE 3.

Moisture content of various types of Brazilian coffee.

(Dried in air oven at 105°C.)

DESCRIPTION OF SAMPLE	RIO NO. 4	RIO NO. 7	VICTORIA NO. 7	RIO AND VICTORIA BLEND	BRAZILIAN BLEND
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Raw	11.3	12.0	9.4	11.8	11.0
Roasted before quenching	----	----	---	1.3	1.23
Roasted and quenched	2.1	3.9	2.0	1.6	1.5
After coating	3.7	7.8	3.7	2.7	1.8

TABLE 4.

Variation in moisture content of coffee stored in 1 pound paper bags.

(Dried in air oven at 105°C.)

DESCRIPTION OF SAMPLE	ANALYZED IN NEW YORK AT TIME OF COLLECTION	STORED AND ANALYZED IN WASHINGTON ABOUT 3 MONTHS AFTER COLLECTION	STORED AND ANALYZED IN NEW YORK 8 MONTHS AFTER COLLECTION	STORED AND ANALYZED IN NEW ORLEANS 6 MONTHS AFTER COLLECTION	STORED AND ANALYZED IN NEW ORLEANS 8 MONTHS AFTER COLLECTION
Green coffees:	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Brazilian blend	11.0	5.86	---	----	----
Rio and Victoria blend	11.8	8.88	---	----	----
Rio No. 7	12.0	5.88	---	----	----
Rio No. 4	11.3	5.93	---	----	----
Victoria No. 7	9.4	5.92	---	----	----
Plain roasted:					
Brazilian blend	1.0	1.96	4.6	4.83	6.24
Rio and Victoria blend	1.6	1.86	4.6	----	----
Rio No. 7	3.9	3.95	---	5.06	6.20
Rio No. 4	2.1	3.09	5.1	4.49	6.34
Victoria No. 7	2.0	2.89	4.6	4.52	6.15
Roasted and coated:					
Brazilian blend	1.5	2.26	4.9	4.79	6.18
Rio and Victoria blend	2.7	3.29	4.9	----	----
Rio No. 7	7.8	5.05	---	6.41	6.43
Rio No. 4	3.7	3.85	4.9	4.91	6.40
Victoria No. 7	3.7	3.96	5.0	5.08	6.31

TABLE 5.

Variation in moisture content of coffee stored in 1 pound paper bags; samples taken from commercial lots analyzed at different periods after collection.

(Dried in air oven at 105°C.)

DESCRIPTION OF SAMPLE	1 MONTH	7 MONTHS	8 MONTHS	9 MONTHS	10 MONTHS
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Roasted and glazed Rio coffee	8.66	6.46	4.72	5.74	6.62
Rio coffee, low grade	5.32	6.21	4.69	5.77	6.50

In connection with a case arising under the Federal Food and Drugs Act, it was desired to determine if the addition of chicory improves in any way the keeping qualities of coffee extract. Several series of hot water extractions of pulverized coffee and coffee-sugar-chicory mixtures were made. Benzoate of soda, and in some instances glycerol, was added, and the number of days before visible mold appeared was recorded. It was found that all extracts of either straight coffee or coffee-sugar-chicory mixture containing benzoate of soda (approximately 0.4 per cent) showed no signs of spoilage in 8 months. Coffee extracts without benzoate of soda spoiled within 9 to 15 days, depending on the concentration. Extracts of mixtures of coffee, chicory and sugar containing

no benzoate spoiled in from 5 to 9 days. Chicory and glycerol (10 per cent) seemed to have no effect upon the keeping quality of the extract.

In Table 6 are given analytical results on some samples of coffee,

TABLE

Analytical results on coffees believed

(Analyzed by H. A. Lepper and

DESCRIPTION	MOISTURE		ASH		ALKALINITY OF ASH		PHOSPHORIC ACID IN ASH	
	Vacuum at 98°C.	Oven at 105°C.	Total	Water-insoluble	Soluble	Insoluble	Soluble	Insoluble
Brazilian:	*per cent*	*per cent*	*per cent*	*per cent*	*cc.*[d]	*cc.*[d]	*per cent*	*per cent*
Raw	6.22[e]	5.86[e]	4.49[e]	1.31[e]	8.15[e]	3.80[e]	0.196	0.176
Plain roast, from cooler	2.43[e]	1.97[e]	4.26	0.79	8.75	3.25	0.202	0.176
Roasted and glazed	2.74[e]	2.26[e]	4.15	0.76	8.50	3.35	0.204	0.167
Rio type No. 7, and Victoria type No. 8:								
Raw	9.45	9.02	4.28[e]	1.09[e]	8.10[e]	3.70[e]	0.177	0.182
Roasted, not quenched	1.17	1.33	4.54	1.05	8.60	3.35	0.234	0.189
Roasted and glazed	3.24[e]	3.29[e]	4.27	0.85	8.25	2.85	0.228	0.172
Rio type No. 7 (large bean):								
Raw	5.83[e]	5.85[e]	4.10[e]	0.89[e]	8.25[e]	3.80[e]	0.183	0.202
Roasted and glazed	5.14[e]	5.11[e]	4.31	0.82	8.35	3.25	0.279	0.165
Plain roast	3.88[e]	3.94[e]	4.31	0.94	8.60	2.95	0.221	0.154
Victoria type No. 7:								
Raw	5.81[e]	5.88	4.15[e]	1.31[e]	7.10[e]	3.45[e]	0.180	0.147
Plain roast	2.99[e]	2.88[e]	4.94	1.86	7.60	3.15	0.145	0.213
Roasted and glazed	3.98[e]	3.96[e]	4.19	1.14	7.50	3.30	0.157	0.185
"Italian Roast" coffee (without oil finish)	4.83	4.82[e]	4.68	0.97	9.00	3.00	0.195	0.194
Victoria, roasted and glazed	4.98[e]	5.01[e]	4.30	0.80	8.60	2.60	0.206	0.189
Rio type No. 4:								
Raw	5.76[e]	5.92[e]	3.81[e]	0.88[e]	7.55[e]	3.55[e]	0.144	0.198
Plain roast	3.06[e]	3.05[e]	4.02	0.94	7.55	3.05	0.123	0.222
Roasted and glazed	3.85[e]	3.85[e]	4.00	0.93	7.75	3.40	0.154	0.221

[a] Nitrogen determined by Mr. T. C. Trescot, Bureau of Chemistry, Washington, D. C.

[b] Extraction made with Johnson extractor instead of Soxhlet, as directed in Gorter method (U. S. Bur. Chem. Bull. 137: 106). Determined nitrogen direct in 50 cc. of 55 cc. filtrate instead of extracting a second time.

[c] Moisture calculation based on the determination in vacuum at 98°C.

believed to be authentic commercial samples, collected from coffee roasters in New York City during October 1914.

In conclusion, it is recommended that the recommendations of the referee for 1915 be carried out, as far as possible, by the referee for 1917.

6.

to be authentic commercial samples.

A. W. Broomell, spring of 1915.)

NITROGEN[a]	ABSOLUTE ETHER EXTRACT	CRUDE FIBER	COLD WATER EXTRACT	CAFFEIN[b]	CALCULATED TO MOISTURE-FREE BASIS[c]				
					Caffein	Nitrogen	Crude fiber	Ether extract	Cold water extract
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
2.07	14.35	18.39	29.82	1.00	1.06	2.20	19.60	15.30	31.79
2.27	14.66	19.90	22.17	1.14	1.16	2.30	20.36	14.99	22.68
2.25	14.63	20.26	21.80	1.16	1.19	2.31	20.81	15.02	22.39
2.18	12.73	16.45[f]	28.53	0.99	1.09	2.40	18.16	14.05	31.50
2.40	14.25	17.13	22.27	1.24[g]	1.25	2.42	17.33	14.41	22.53
2.30	13.79	16.62	22.95	1.13	1.16	2.37	17.17	14.25	23.71
2.11	12.85	14.90	29.98	1.03	1.09	2.24	15.82	13.64	31.83
2.18	13.03	17.83	21.53	1.22	1.28	2.29	18.79	13.73	22.69
2.26	14.05	17.26	21.62	1.31	1.36	2.35	17.95	14.61	22.49
2.04	14.19	17.85	27.45	0.87	0.92	2.16	18.95	15.06	29.14
2.19	15.37	16.96	22.06	1.09	1.12	2.25	17.48	15.84	22.74
2.15	15.00	15.77	22.19	1.14	1.18	2.23	16.40	15.60	23.08
2.25	15.43	14.08	23.83	1.11	1.16	2.36	14.79	16.21	25.03
2.15	14.42	14.98	22.57	0.98	1.03	2.26	15.76	15.17	23.75
2.18	14.54	16.15	30.49	1.08	1.14	2.31	17.13	15.42	32.35
2.35	14.43	16.90	22.64	1.24	1.28	2.42	17.43	14.88	23.35
2.38	14.25	16.11	22.59	1.25	1.30	2.47	16.75	14.82	23.49

[d] N/10 per 2 gram sample.
[e] Analysis made by A. W. Broomell, Bureau of Chemistry, Washington, D. C.
[f] Determination made by G. P. Walton, Cattle Food Laboratory, Bureau of Chemistry, Washington, D. C.
[g] Gravimetric determination.

REPORT ON PRESERVATIVES.

By A. F. SEEKER[1] (Bureau of Chemistry, Food and Drug Inspection Station, New York, N. Y.), *Associate Referee.*

Following the recommendations adopted at the last meeting, the work for this year has consisted principally of a trial of certain methods for the determination of saccharin. The method given in Bureau of Chemistry Bulletin 107 (Revised), page 183, is somewhat vague and lacking in details, but its revised form[2] has been found by the referee to be satisfactory and sufficiently accurate in most cases. It is inaccurate, however, in the presence of ether-soluble sulphur compounds, and in many cases, as pointed out by Gnadinger[3], the solution prepared as directed gives rise to troublesome emulsions during extraction. These defects Gnadinger proposes to overcome by treatment of the solution with lead acetate before extraction to precipitate emulsion-forming substances, and the removal of ether-soluble sulphur compounds from the extracted residue by treatment with petroleum ether and later with bromin.

The methods selected for trial were substantially those proposed by Gnadinger at the last meeting, the details being as follows:

METHOD I. DETERMINATION OF SACCHARIN IN THE ABSENCE OF OTHER ETHER-SOLUBLE SULPHUR COMPOUNDS.

PREPARATION OF SOLUTION.

Fruit juices, sirups and similar liquid preparations.—Transfer 100 grams of the sample to a 250 cc. volumetric flask by means of a little water, dilute to about 200 cc. with water, add 5 cc. of glacial acetic acid, mix, add a slight excess of 20% neutral lead acetate solution, mix thoroughly, dilute to the mark with water, again mix thoroughly and filter through a folded filter.

Solid or semi-solid preparations.—Transfer 50 grams of the sample to a 250 cc. volumetric flask by means of a little hot water and add sufficient nearly boiling water to make the volume about 200 cc. Allow the mixture to stand for 2 hours, shaking occasionally. Then add 5 cc. of glacial acetic acid, mix thoroughly, add a slight excess of 20% neutral lead acetate solution, dilute to the mark with cold water, mix, and allow to stand for 20 minutes. Filter through a folded filter.

EXTRACTION AND DETERMINATION.

Transfer 150 cc. of the filtrate to a separatory funnel, add 15 cc. of concentrated hydrochloric acid and extract three times with 80 cc. portions of ether, shaking the separatory for 2 minutes each time. Wash the combined ether extracts once with 5 cc. of water, remove the ether by distillation and transfer the residue to a platinum crucible by means of a little ether, or if substances difficultly soluble in ether are present, use alternate small portions of water and ether. Evaporate the ether on a steam bath,

[1] Since deceased.
[2] *Assoc. Official Agr. Chemists, Methods*, 1916, 145.
[3] *J. Assoc. Official Agr. Chemists*, 1917, **3**: 25.

add 2–3 cc. of a 10% sodium carbonate solution to the residue, rotate so that all of the residue is brought into contact with the solution and evaporate to dryness on a steam bath. To the dry residue in the crucible add 4 grams of a mixture of equal parts of anhydrous sodium and potassium carbonates, heat gently at first and then to complete fusion for 30 minutes over an alcohol or other sulphur-free flame. The fusion may be conducted with a gas flame by closely fitting the crucible into a hole cut into a piece of heavy asbestos board so that one-third of the crucible projects above the asbestos, and heating the lower portion of the crucible by means of a large Bunsen or Meker burner. Cool, dissolve the melt in water, add about 5 cc. of bromin water, acidify with hydrochloric acid, filter, wash the paper with a little water, dilute the filtrate and washings to about 200 cc., heat to boiling and slowly add an excess of barium chlorid solution. Allow the mixture to stand 5–6 hours, or better, overnight, separate the precipitated barium sulphate by filtration, wash until free from chlorids, dry, ignite, cool and weigh. Correct the result thus obtained for any sulphur present in the fusion mixture as found by a blank determination. Calculate the equivalent amount of saccharin by multiplying the corrected weight of barium sulphate by 0.7845.

NOTE.—Instead of the mixed sodium and potassium carbonates, 3–4 grams of sodium peroxid may be employed for the fusion. In this case, a nickel crucible must be used and the time of fusion may be reduced to 5 minutes. The separation of a little lead chlorid during the extractions does not interfere with the accuracy of the method.

METHOD II. DETERMINATION OF SACCHARIN IN THE PRESENCE OF MUSTARD OIL.

PREPARATION OF SOLUTION.

Prepare the solution as directed under "Method I, solid or semi-solid preparations".

EXTRACTION AND DETERMINATION.

Transfer 150 cc. of the filtrate, obtained as directed under "Preparation of Solution", to a separatory funnel, add 15 cc. of concentrated hydrochloric acid and extract three times with 80 cc. portions of ether, shaking the separatory for 2 minutes each time. Wash the combined ether extracts once with 5 cc. of water and transfer the ether to a 250 cc. beaker. Add about 10 grams of washed sea sand and evaporate the ether before a fan or air blast. Distribute the sand on the walls of the beaker with a stirring rod and continue the spontaneous evaporation until quite dry. Add 25 cc. of petroleum ether (b. p. 30–65°C.), and rub thoroughly with a "policeman". Decant through a dry 7 cm. quantitative paper and repeat the washing twice, using 25 cc. of petroleum ether each time. Reject the petroleum ether washings and return the filter paper to the beaker containing the sand. Wash the residue on the sand with hot water and filter into a separatory funnel, collecting about 75 cc. of the filtrate. Cool, add 7–8 cc. of concentrated hydrochloric acid and a distinct excess of bromin water, allow to stand for 5 minutes and destroy the excess of bromin with sodium nitrite solution, avoiding a large excess of the latter. Extract the acid solution three times with 50 cc. portions of ether, and wash the combined ether extracts once with 5 cc. of water. Evaporate the ether, subject the residue to alkaline fusion, and precipitate barium sulphate in an acidified solution of the melt, as directed under Method I, beginning with "Cool, dissolve the melt in water, etc." Multiply the corrected weight of barium sulphate found by 0.7845 to obtain the equivalent weight of saccharin, and add 0.5 mg. to this result to correct for the saccharin dissolved by the petroleum ether.

A preliminary trial of these methods by the referee gave the results shown in Table 1.

TABLE 1.

Results of determinations of saccharin by Methods I and II.

SUBSTANCE	METHOD	SACCHARIN ADDED	SACCHARIN FOUND	RECOVERY
		per cent	*per cent*	*per cent*
Raspberry jam	I	0.050	0.048	96
Sweet pickles	I	0.075	0.069	92
Cider	I	0.020	0.019	95
Ketchup	I	0.100	0.092	92
Ketchup	I	0.050	0.049	98
Chow chow	II	0.050	0.043	86
Chow chow	II	0.050	0.046	92
Chow chow	II	0.100	0.082	82
Chow chow	II	0.100	0.088	88

The results given in Table 1 show an average recovery by Method I of 95 per cent and of 87 per cent by Method II. The results obtained by similar methods as reported by Gnadinger at the last meeting were: Average recovery, Method I, 99 per cent; and Method II, 92 per cent. The success of the preliminary work warranted submitting these methods to further trial by the collaborators.

Accordingly, three mixtures were prepared and sent to the various collaborators, together with the details of the methods as given above. The substances selected for the test were of such a character as to represent as nearly as possible the different types in which saccharin is commonly found, and which would present the ordinary difficulties of accurate determination, but which would, at the same time, allow the saccharin to be uniformly distributed throughout the sample so that the portion taken by each analyst for the determination would contain the same amount of the substance sought.

The first mixture consisted of strawberry sirup prepared by the referee from strawberry juice and cane sugar to which 0.066 per cent of saccharin was added. The second mixture consisted of a commercial tomato puree, in which no saccharin was found by a blank determination, to which 0.066 per cent of saccharin was added by the referee together with 0.5 per cent of boric acid to prevent decomposition before analysis. The third mixture consisted of a finely ground mustard relish prepared by the referee from cucumbers, onions, cauliflower, red pepper, curry powder, salt and vinegar, 0.099 per cent of saccharin being added to the finished product.

The results obtained by the ten collaborators as given in Table 2 were reported by: (1) S. Adler, U. S. Bureau of Animal Industry. Federal Building, Kansas City, Kans.; (2) C. B. Gnadinger, U. S. Food and Drug Inspection Station, Transportation Building, Chicago, Ill.; (3) M. E. Hinds, Food and Drug Department, Nashville, Tenn.; (4) L. Katz, U. S. Food and Drug Inspection Station, U. S. Appraiser's

Stores, New York, N. Y.; (5) H. B. Mead, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, Philadelphia, Pa.; (6) L. C. Mitchell, U. S. Food and Drug Inspection Station, Old Custom House, St. Louis, Mo.; (7) M. B. Porch, H. J. Heinz Company, Pittsburgh, Pa.; (8) W. D. Richardson, Swift & Company, Chemical Laboratory, Chicago, Ill.; (9) M. G. Wolf, U. S. Food and Drug Inspection Station, U. S. Appraiser's Stores, New York, N. Y.; and (10) P. B. Yost, U. S. Food and Drug Inspection Station, U. S. Custom House, New Orleans, La. To all of these collaborators the referee wishes to express his acknowledgments for their valuable cooperation.

TABLE 2.

Results obtained by collaborators on samples submitted by referee.

ANALYST	METHOD I				METHOD II	
	STRAWBERRY SIRUP (CONTAINED 0.066 PER CENT OF SACCHARIN)		TOMATO PUREE (CONTAINED 0.066 PER CENT OF SACCHARIN)		MUSTARD RELISH (CONTAINED 0.099 PER CENT OF SACCHARIN)	
	Amount found	Recovery	Amount found	Recovery	Amount found	Recovery
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
(1)	0.070	106	0.066	100	0.076	77
	0.068	103	0.072	109	0.072	73
	0.049	74	0.067	102	0.073	74
(2)	0.052[a]	79	0.062	94	0.083	84
	0.058[a]	88	0.065	99	0.088	89
(3)	no sample		no sample		0.070	71
					0.070	71
(4)	0.062	94	0.065	99	0.088	89
	0.050	76	0.062	94	0.088	89
	----	---	----	---	0.084	85
(5)	0.062	94	0.065	99	0.070	71
	0.065	99	----	---	0.075	76
(6)	0.059	89	0.048	73	0.070	71
	0.060	91	0.053	80	0.052	53
(7)	0.063	96	0.042	64	no sample	
	0.065	99	0.050	76		
(8)	0.049[a]	74	0.062	94	0.076	77
	0.050[a]	76	0.056	85	0.072	73
(9)	0.058	88	0.064	97	0.092	93
	0.055	83	0.059	89	----	--
(10)	0.066	100	0.067	102	0.083	84
	0.067	102	0.069	105	0.080	81

[a] Sample badly fermented.

COMMENT BY COLLABORATORS.

C. B. Gnadinger.—The results obtained on Sample 1 (strawberry sirup) were not satisfactory. From the experience I have had with the method, I am led to believe that this is due to the manner of preparing the extracted saccharin for fusion. When ether is evaporated from a crucible on a steam bath, as directed in the method, there will be some loss by spattering; moreover, the contents of the crucible have a tendency to creep over the edge and to form a ring at the top of the crucible. It is difficult to prevent loss of this material. During the extraction a large amount of acetic acid is taken up by the ether and remains (in Method I) after the ether is distilled. It was found that 3 cc. of 10% sodium hydroxid were not sufficient to neutralize this acid. If the acid solution is evaporated to dryness, saccharin may be lost; if sufficient alkali is added to neutralize the acid, the evaporation requires a long time. In the case of Sample 2 (tomato puree), sufficient sodium carbonate was added to make the solution alkaline before evaporating. In every case it was necessary to filter the solution of the melt, even when platinum crucibles were used. The procedure given below is that used in developing the method as reported at the last meeting of the association. This procedure should have been given as part of the method, but was omitted through the fault of the writer. Other analysts and I have examined a number of samples with excellent results.

Proceed as in Method I to "Wash the combined ether extracts once with 5 cc. of water". Transfer the ether to a beaker and evaporate to dryness before a fan or air blast. Dissolve the residue in about 5 cc. of alcohol, add phenolphthalein and about 5 cc. excess of approximately N/10 sodium hydroxid. Transfer to a 40 cc. nickel crucible with hot water, rinsing the beaker three times. Evaporate on a steam bath until only 1–2 cc. remain. Weigh out 5 grams of fusion mixture (6 parts of sodium carbonate and 1 part of potassium nitrate), carefully rotate the crucible so that the entire inner surface is moistened, and with a spatula add part of the fusion mixture, completely covering the moistened wall of the crucible. Finally scrape the material from the wall to the bottom of the crucible and cover with the rest of the fusion mixture. Cover the crucible and heat gently for about 5 minutes and then fuse for 25 minutes. Cool, place the crucible in a 250 cc. beaker, cover with cold water and add 15 cc. of concentrated hydrochloric acid. Let stand until the melt is dissolved, filter through a quantitative paper, neutralize with ammonium hydroxid and add 1 cc. excess of concentrated hydrochloric acid. Heat to boiling and add slowly with constant stirring an excess of boiling barium chlorid solution; continue the boiling several minutes and let stand overnight. Collect the precipitate on a weighed Gooch crucible and wash thoroughly with boiling water. Dry, ignite, cool and weigh. Correct the result thus obtained for any sulphur present in the fusion mixture, as found by a blank determination. Calculate the equivalent amount of saccharin by multiplying the corrected weight of barium sulphate by 0.7844.

The three samples submitted by the associate referee were examined by this procedure and the results are given herewith:

STRAWBERRY SIRUP[a]	TOMATO PUREE	MUSTARD RELISH
per cent	*per cent*	*per cent*
0.066	0.082	0.092
0.067	0.075	0.088
0.068	0.077	0.091

[a] Sample badly fermented.

L. Katz.—Shaking for 30 seconds instead of 2 minutes was tried and found to give somewhat lower results: Strawberry sirup, 0.047 per cent; and tomato puree 0.060, per cent.

H. B. Mead.—The method, while somewhat tedious, proceeds smoothly. From my experience in using immiscible solvents, I believe it is unnecessary to shake the extractions for 2 minutes. Accordingly all extractions in the first determination in each case were shaken for 2 minutes. The first extraction in the second determination in each case was shaken for 2 minutes, the second and third extractions for 30 seconds each.

L. C. Mitchell.—An electric muffle was used in fusing the sodium and potassium carbonates. The platinum crucibles were put into a cold muffle, the current turned on, the temperature raised gradually to complete fusion of the carbonates, and kept at this temperature for 30 minutes. The following method for the determination of saccharin was tried:

Transfer 100 grams of the sample to a 250 cc. flask by means of a little water, dilute to about 200 cc. with water, make distinctly alkaline to litmus paper with strong sodium hydroxid solution, mix thoroughly, dilute to the mark with water, again mix thoroughly, let stand at least 2 hours and filter through a folded filter. Transfer 150 cc. of the filtrate to a separatory funnel, add 15 cc. of concentrated hydrochloric acid and extract with 100, 50, 50, and 50 cc. portions of a 1 to 1 mixture of ether and petroleum ether (b. p. 30–60°C.). Shake carefully for 2 minutes each time. Wash the combined ether petroleum ether extracts once with 5 cc. of water, and allow the ether to evaporate spontaneously. Add 25 cc. of neutral 95% alcohol and titrate with sodium hydroxid (1 cc. equivalent to 1 mg. of saccharin), using phenolphthalein as indicator.

The following results were obtained: Strawberry sirup, 0.048 per cent; tomato puree, 0.045 per cent; and mustard relish, 0.090 per cent.

The titrated liquids were in each case then subjected to the fusion procedure. Samples 1 and 2 as follows: After titrating add 5 cc. of a 10% sodium carbonate solution, evaporate nearly to dryness on a steam bath, transfer to a platinum crucible by means of a little hot water, and evaporate to dryness on a steam bath. Then continue as in Method I. The results obtained were: Strawberry sirup, 0.044 per cent; tomato puree, 0.039 per cent. Sample 3 (mustard relish) was treated as follows: After titrating add 10 grams of washed sea sand, evaporate to dryness on a steam bath, distributing the sand on the sides of the evaporating dish with a stirring rod before complete dryness is reached. Add 25 cc. of petroleum ether and continue as in Method II. The result obtained was 0.077 per cent. Duplicate determinations were not made, owing to the lack of sufficient sample.

M. G. Wolf.—Two methods in addition to those submitted by the referee were tried. One of these is based upon the determination of saccharin by means of its nitrogen content and in the other the saccharin is weighed as such. The first method is as follows:

Extract the saccharin as directed in Method I, proceeding to the point at which the impure saccharin is recovered from the ether solution, as indicated by the words, "Wash the combined ether extracts once with 5 cc. portions of water, remove the ether by distillation". Transfer the residue to a 50 cc. beaker by means of a little ether and evaporate the ether on a steam bath. Add 10 cc. of water to the residue in the beaker, heat the covered beaker on a steam bath for 5–10 minutes, add 0.05–0.10 gram of sodium acetate and, when this has dissolved, cool and add 10 cc. of alcohol and 0.5 cc. of a saturated aqueous solution of silver nitrate. Allow the mixture to stand overnight, collect the precipitate on a Gooch crucible and wash with 40–50 cc. of alcohol in small portions at a time. Dry the crucible in a water oven, and then transfer the asbestos pad with the precipitate to an Erlenmeyer flask. Add sufficient water to the flask to make the volume of liquid about 100 cc., then add 10 cc. of concentrated hydrochloric acid for each 90 cc. of liquid, insert a short-stemmed funnel into the neck of the flask and boil gently for 45 minutes. Filter through a Gooch and wash with hot water, collecting the filtrate and washings in a porcelain dish. To the combined filtrate and washings, add an amount of platinic chlorid solution equivalent to 0.2–0.3 gram of $PtCl_4$ (in case a large amount of extractive matter remains after

removing the ether, use 0.5 gram) and evaporate on a steam bath to a pasty consistency. Then add about 25 cc. of 80% alcohol, collect the precipitate of ammonium platinic chlorid on a Gooch, wash with 80% alcohol, dry at 100°C., cool and weigh. Wash the residue on the Gooch repeatedly with hot water to remove the ammonium platinic chlorid, finally wash with a little 95% alcohol, dry at 100°C., cool and weigh. The difference between the first and second weighings is the weight of the ammonium platinic chlorid obtained from the decomposition of the saccharin. Multiply this weight by 0.825 to obtain the equivalent of saccharin.

Method in which the saccharin is weighed as such:

Proceed as in the foregoing method to the point indicated by the words, "Allow the mixture to stand overnight, collect the precipitate on a Gooch crucible and wash with 40–50 cc. of alcohol in small portions at a time". After completing the operation just mentioned, wash with three small portions of ether, dry in a water oven, and transfer the asbestos pad and the precipitate to a beaker. Add 50 cc. of water and sufficient bromin water to produce a strong coloration, and heat on a steam bath with frequent stirring for about 10 minutes. Filter through a Gooch crucible, and wash with successive small portions of hot water until the volume of the filtrate measures 100–120 cc. Cool the combined filtrate and washings, transfer to a separatory funnel, add sufficient sodium bisulphite to destroy the excess of bromin, add 5 cc. of concentrated hydrochloric acid for each 100 cc. of liquid, and extract four times with washed ether, using for each extraction a volume of ether equivalent to half the volume of the aqueous layer. Wash the four ether extracts in succession with two 5 cc. portions of water, transfer the ether solution to a flask, distil off the solvent, then transfer the residue by means of a little ether to a small tared dish, evaporate the ether on a steam bath, and dry the residue of saccharin to constant weight at 100°C.

The result obtained by the first method on the tomato puree was 0.057 per cent of saccharin, and by the second method on the strawberry sirup, 0.064 per cent of saccharin.

DISCUSSION OF RESULTS.

Taking into account the small amount of saccharin present in the samples, which would tend to magnify ordinary errors when results are compared upon the basis of percentage yield, it is considered that a recovery of saccharin coming within 15 per cent of the actual amount present may be regarded as within the permissible limit of error. Upon this basis and by disregarding those results in which the strawberry sirup was badly fermented when analyzed, it is found that, in the case of the strawberry sirup, twelve of the fifteen results reported and, in the case of the tomato puree, fourteen of the eighteen results reported, may be accepted as satisfactory, all of these having been obtained by Method I as submitted by the referee. The majority of these results (twenty-two out of thirty-three) come well within a 10 per cent limit of error. The method may therefore be accepted as satisfactory.

With regard to Method II, only five of the nineteen results reported come within the 15 per cent limit of error. The results are all low, and with the exception of one, which may be disregarded, show a yield of 71 to 93 per cent of the actual amount present. It appears that some source of error exists, and further work should be done upon this method to ascertain whether the details suggested by C. B. Gnadinger in this report or other modifications will correct its defects.

It is desirable that a method for the determination of saccharin other than one based upon its sulphur component be found for purposes of

confirmation, in order that in contested cases the findings may be placed upon an unassailable basis. Owing to the great amount of time demanded by the associate referee's duties as a member of the Committee on Editing Methods of Analysis, it was found impossible to continue the work done last year along this line. For this purpose, methods such as those proposed by M. G. Wolf in this report should be investigated.

Another feature of the work still remaining unsolved is the determination of saccharin in baked flour preparations of the nature of ice cream cones, the difficulties of which were pointed out last year.

RECOMMENDATIONS.

It is recommended—

(1) That Method I, as given in this report, for the determination of saccharin in the absence of other ether-soluble sulphur compounds be adopted as a tentative method in place of the existing provisional method.

(2) That further work be done on Method II for the determination of saccharin in the presence of mustard oil, that other methods not dependent upon the sulphur component of saccharin be investigated, and that further work be done upon the determination of saccharin in baked flour preparations.

SALICYLIC ACID.

The attention of the associate referee has several times been called to the fact that only one qualitative test for salicylic acid is given in Bureau of Chemistry Bulletin 107 (Revised), and that this in some instances may lead to erroneous findings. It has been the experience of the referee that the ferric chlorid test there given is not characteristic for salicylic acid, and that a similar reaction is given by the residue from the ether extract of roasted or caramelized cereal products. Others have observed the same fact, as shown by reference to the literature: Abraham[1]; Erich[2]; Brand[3]; Munsche[4]; Backe[5]; Sherman[6]; Sherman and Gross[7].

The reaction proposed by Jorissen[8] has been in use in the New York Food and Drug Inspection Station of the Bureau of Chemistry for several years, and has proved very satisfactory as a confirmatory test. The method was first published in 1882 and has been favorably reported at various times since then: Klett[9]; Windisch[10]; da Silva[11]; Portes and

[1] Abst. *Z. Nahr. Genussm.*, 1898, **1**: 857.
[2] *Bierbauer*, 1893, **24**: 465.
[3] *Z. ges. Brauw.*, 1893, **16**: 303; *Ber.*, 1894, **27**: 806.
[4] *Wochschr. Brauerei*, 1893, **10**: 739.
[5] *Compt. rend.*, 1910, **150**: 540; 1910, **151**: 78.
[6] *J. Ind. Eng. Chem.*, 1910, **2**: 24.
[7] *Ibid.*, 1911, **3**: 492.
[8] *Bull. acad. roy. Belg.*, 1882, 3rd ser., **3**: 259.
[9] *Pharm. Centrh.*, 1900, **41**: 452.
[10] *Z. Nahr. Genussm.*, 1903, **6**: 447.
[11] *Compt. rend.*, 1900, **131**: 423.

Desmoulières[1]; Sherman[2]; Sherman and Gross[3]. C. L. Black of the Philadelphia Food and Drug Inspection Station of the Bureau of Chemistry, also reports favorably on the test. It has been stated by several of those who have used the test that the reaction is distinct when as little as 0.05 mg. of salicylic acid is present in 10 cc. of the solution tested. This has been confirmed by the referee, who also finds that, with the exception of coloring matter, none of the substances ordinarily present in the ether extracts of foods interfere with the test, and no interfering substance is to be expected if the salicylic acid is purified in the usual way. Special interest is to be attached to the fact that neither benzoic nor cinnamic acids give the test.

The reaction is performed as follows:

Extract the salicylic acid as directed in the tentative method[4]. Dissolve the purified salicylic acid in hot water, cool 10 cc. of the solution in a test tube, add 4 or 5 drops of a 10% potassium nitrite solution, 4 or 5 drops of 50% acetic acid and 1 drop of 10% cupric sulphate solution, mix thoroughly and heat to boiling. Boil for 30 seconds and allow to stand for 1–2 minutes. In the presence of salicylic acid a blood red color will develop.

Taking into consideration the length of time this test has been in use, the numerous favorable reports in the literature and the experience reported by the New York and Philadelphia Food and Drug Inspection Stations of the Bureau of Chemistry, together with the need of an official confirmatory test to supplement the findings by the ferric chlorid reaction, which alone may prove misleading, it is recommended that the Jorissen test as here given be tentatively adopted.

Messrs. H. D. Gibbs[5] and G. A. Geiger[6] (Bureau of Chemistry, Washington, D. C.) presented a paper on "The Manufacture of Benzaldehyde with Benzoic Acid as a By-Product".

REPORT ON METALS IN FOOD.

By DAVID KLEIN[7] (Division of Foods and Dairies, Illinois Department of Agriculture, 1410 Kimball Building, Chicago, Ill.),
Associate Referee.

The work was confined to the study of the Gutzeit method for arsenic, and its application to specific foods. It was also intended to study the methods for the determination of tin. This part of the work was unfortunately interrupted when the chemist who was assigned the problem

[1] *Ann. chim. anal.*, 1901, 6: 401.
[2] *J. Ind. Eng. Chem.*, 1910, 2: 24.
[3] *Ibid.*, 1911, 3: 492.
[4] *Assoc. Official Agr. Chemists, Methods*, 1916, 141.
[5] Present address, Jackson Laboratory, E. I. Du Pont Co., Wilmington, Del.
[6] Present address, 43 Gaston Street, West Orange, N. J.
[7] Present address, Hollister-Wilson Laboratories, Chicago, Ill.

was called out with the troops. The work has recently been resumed, but nothing can be reported at this time.

In view of the very unsatisfactory and conflicting results reported by previous collaborators on the Gutzeit method, it was decided not to send out any samples until the method was subjected to close scrutiny, and the doubtful directions revised. To that end Mr. J. J. Doyle (Illinois Division of Foods and Dairies, Chicago, Ill.) has devoted most of his time during the past nine months. Certain changes in the previous procedure can be reported now, which should lead to more accurate and uniform results in the hands of different chemists.

One of the changes is the use of Munktell's No. 00 filter paper in place of Whatman's cold pressed paper for making the stains. With the latter paper it was not possible to obtain stains of equal density or length on both sides of the paper. The results were erratic and unsatisfactory. Munktell's No. 00 paper was selected after trying several kinds of hard and soft papers. With this paper it is not difficult to obtain easily reproducible stains of equal density and size on both sides of the paper.

The width of the test paper should be that of the diameter of the tube, rather than slightly smaller. With a paper narrower than the tube, there was a tendency to curl, causing a deflection of the gas current and an unevenness of deposit. Great care should be taken in getting tubes of the same diameter. In our work, the tubes had a diameter of $\frac{1}{8}$ inch.

The best concentration of sensitizing solution was found to be 1.5 per cent mercuric bromid solution. In preparing the test paper, blotting the excess liquid was found unsatisfactory. Better results were obtained by allowing the papers to dry in the air.

For generating the hydrogen and the arsine, sulphuric and hydrochloric acid yield identical results. The concentration of the acid, if sulphuric is used, should be 3 to 4 cc. of acid (sp. gr. 1.84) in 40 cc. of total liquid; if hydrochloric is used, 4 to 8 cc. of acid (sp. gr. 1.20) in 40 cc. of total liquid.

The presence of tin and iron in the reacting liquid was thoroughly investigated. Stannous compounds are essential. When stannous chlorid was omitted, not only was the evolution of arsine slow, but it was also very incomplete. Since the injurious effect of ferric iron has been well established, no work was done on it. The literature on the influence of ferrous iron is conflicting. Our experiments indicate that the presence of ferrous iron hastens the complete evolution of the arsine, but is without influence on the final amount evolved. For this reason a small amount of ferrous iron is added, which is further treated with stannous chlorid to insure its complete existence in that state. The presence of potassium iodid offers no advantage in the procedure. Its use was discontinued.

In the construction of the apparatus, the coil of filter paper was replaced by cotton moistened with a 20 per cent lead acetate solution.

The temperature of the reacting solution should be more accurately controlled than was formerly the case. Immersion of the bottles in water maintained at about 25°C. throughout the reaction was found to be a convenient method of controlling the temperature and securing a uniform evolution of arsine.

A method was devised for estimating the amount of arsenic in an unknown stain without a direct comparison with standard stains. Inasmuch as the standards do not keep well and are troublesome to handle, the suggested method simplifies the determination without any loss of accuracy. Differences of 0.5 microgram are readily detected. Advantage is taken of the fact that the upper limits of the stains for correspondingly increasing amounts of arsenic lie upon a straight line. If, therefore, the slope of this line is determined and the line drawn to correct scale, the amount of arsenic on any test paper can be quickly ascertained by superimposing it on the scale at the point where the upper limit of stain coincides with the straight line. In place of using the extreme limit of coloration as the basis of comparison, a point slightly below this has been chosen arbitrarily, where the dark brown abruptly changes into the pale yellow.

As applied to foods, the method was thoroughly tested on a phosphate starch mixture used as part of the ingredients in baking powder. Despite the disadvantages and inconvenience of a wet digestion method, we have not found a method superior to it. Work along this line is still in progress, but all results herein reported were made after destroying the organic matter with nitric and sulphuric acid. The often quoted precaution of avoiding high temperatures during the digestion was subjected to considerable study. It was found that the loss of arsenic through volatilization, if it occurred at all, was too slight to be detected. This is also true, even if the product contains a large amount of chlorid. For these reasons no special precautions were deemed necessary in the maintaining of definite temperatures during the digestion.

METHOD FOR THE DETERMINATION OF ARSENIC.

(Adapted from method of C. R. Smith[1].)

REAGENTS.

Concentrated nitric acid and concentrated sulphuric acid.—Must be arsenic-free.

Zinc.—Arsenic-free stick zinc broken in pieces to weigh about 10 grams. The zinc may be used again if its surface remains crystalline. After a test, wash the zinc in distilled water, let it dry on filter paper.

---

[1] U. S. Bur. Chem. Circ. 102; *J. Soc. Chem. Ind.*, 1907, 26: 1115; Original Contributions, Eighth Intern. Cong. Appl. Chem., 1912, 1: 9.

Lead acetate cotton.—Absorbent cotton, part of which is soaked in 5% lead acetate solution, and part in 20% solution. Squeeze out excess moisture.

Mercuric bromid paper.—Immerse 15 cm. Munktell's No. 00 filter paper in the solution contained in a tall, narrow beaker. Allow the paper to remain a few minutes. Slowly draw it out of the liquid, touching the paper to the side of the beaker. Place the paper on a flat surface so that the paper forms a convex arch. Allow it to dry thoroughly. With a photo-trimmer or other suitable device, cut the test papers to fit the tubes as accurately as possible. Reject all outside portions of the original paper. Before placing the paper in the tube, cut off about 1 cm. from one end of the paper. The freshly cut edge should form the base of the test paper. The 1 cm. strip can be used as indicated in the directions.

Stannous chlorid solution.—Forty grams of the crystals made up to 100 cc. with concentrated hydrochloric acid and water.

Standard arsenic solution.—Dissolve 1 gram of arsenious oxid in 25 cc. of 20% sodium hydroxid, neutralize with dilute sulphuric acid. Add 10 cc. of concentrated sulphuric acid and dilute to 1 liter with recently boiled distilled water.

1 cc. of this solution contains 1 mg. As_2O_3.

Dilute 20 cc. of this solution to 1 liter. Make 50 cc. of the dilute solution up to 1 liter. Each cc. of the latter solution contains 0.001 mg. of arsenic trioxid. This solution is used to make the standards. The dilute solutions should be made up freshly when required.

Ferrous ammonium sulphate.—Dissolve 30 grams of the crystals in water, slightly acidified with sulphuric acid; then dilute to 100 cc.

APPARATUS.

The generator is a 2 ounce wide-mouthed bottle. This is connected by means of a rubber stopper to a glass tube, 1 cm. × 6 cm., loosely filled with the absorbent cotton soaked in 20% lead acetate solution. It is advisable not to pack the lower end of the tube, thus preventing the liquid carried up by the gas bubbles from acting on the lead acetate. This lower tube is connected with a similar one, loosely packed with cotton soaked in 5% lead acetate solution. The cotton should be uniformly moist in all tubes. The second tube is connected with a capillary tube exactly 3 mm. in internal diameter and about 12 cm. in length. It is advisable to smooth the upper end of this tube by filing rather than fire-polishing it, unless the latter is very carefully done, so as to prevent reduction of the diameter. The sensitized mercuric bromid paper is carefully placed in this upper tube with the freshly cut end downward. All connections are made with rubber stoppers which should be free from any white coating.

PREPARATION OF THE STANDARDS.

Into each generator bottle put about 40 cc. of sulphuric acid solution containing 3.5 cc. of concentrated acid. Add 0.5 cc. each of the stannous chlorid and ferrous ammonium sulphate solutions. Add the requisite amount of the standard arsenic solution to each generator bottle, so that the stains will represent 0.5, 1, 1.5, 2, 3, 4, 6, 8, 10 micrograms of As_2O_3. Keep the bottles in a water bath at 90°C. for about 10 minutes. Test a drop of the solution for ferric iron with potassium sulphocyanate. If no ferric iron is present, place the bottles in a water bath at 25°C. Allow sufficient time for the bottles to attain that temperature. Add 2 pieces of stick zinc about 1 inch long. Immediately attach the rest of the generating apparatus, into the upper tube of which the test paper has been fitted. Maintain the water in the bath at

25°C., and allow the reaction to proceed for about 45 minutes. At the end of that time, remove the test papers, and put in short lengths of fresh papers, to make sure that the evolution is complete. Allow the papers to dry in the air for a few minutes; then immerse them for a moment in melted paraffin.

On properly ruled cross section paper, with the width of the strips as the abscissa, place the strips in serial order, leaving the necessary intervals for the concentrations lacking to make a complete series separated by 0.5 microgram. If the series is properly prepared, the upper edge of the stains should lie upon a straight line. Instead of using the extreme upper color limit, it has been found simpler to select a region slightly below this, where the darker color seems to change abruptly into a pale yellow. This point on the 0.5 and 10 microgram stains should be marked on the cross section paper. Through these points draw a straight line.

Draw vertical lines to intersect the slanting line, at 0.5 microgram intervals. The amount of arsenic on any unknown strip may be read directly from this scale by placing the strip in the proper place, so that the upper edge of the dark coloration will coincide with the scale.

After the scale has been established, the standard stains need not be retained. It is not advisable to work with quantities giving stains of more than 10 micrograms.

DETERMINATION OF ARSENIC IN BAKING POWDER AND BAKING POWDER CHEMICALS CONTAINING ORGANIC MATTER.

Weigh 10 grams of powder into a dry 4 inch porcelain casserole. Add 10 cc. of nitric acid (sp. gr. 1.42). Cover the casserole with a watch glass and warm gently on a steam bath until the starch is hydrolyzed and nitration begins. Remove from the bath, and set aside until the violent reaction is over. Then add 8 cc. of sulphuric acid (sp. gr. 1.84) and heat on a steam bath for about 30 minutes. Continue the heating on a hot plate until the liquid turns dark brown, but avoid an excessive charring. Remove from the hot plate, add 2 cc. of nitric acid and heat again until the appearance of charring. Repeat the addition of nitric acid and subsequent heating until there is no sign of charring after the nitric acid is driven off. There should be a slightly yellow solution with a mass of calcium sulphate.

When the destruction of organic matter is complete, remove the casserole from the hot plate, wash down the contents with 50–60 cc. of water, and evaporate first on a steam bath, then on a hot plate until fumes of sulphur trioxid appear. Remove from the bath and repeat the operation until all of the nitric acid is driven off. This may be determined by adding a drop of the liquid to a drop of diphenylamin sulphate solution (40–50 mg. in 2 cc. of concentrated sulphuric acid) on a porcelain plate. If nitric acid is present the mixture will turn blue. This test is extremely delicate, a blue color often resulting from air contamination.

Transfer the contents of the casserole to a 100 cc. volumetric flask. Make up to the mark; let the precipitate settle and pipette 50 cc. of the supernatant liquid into a Gutzeit generator bottle. Add 1.5–2 cc. of stannous chlorid solution and proceed as directed when making the standards. It may happen that the amount of stannous chlorid is not sufficient to reduce the iron. In that case add 1 cc. of stannous chlorid and repeat until all iron is reduced. In the presence of large amounts of phosphates and sulphates, the potassium thiocyanate is seldom colored red by traces of ferric iron. A light brown or straw color usually results.

Estimate the amount of arsenic on the test paper by superimposing it on the proper place of the scale. Paraffining the test paper aids in its keeping quality, especially if it is kept in a cool, dark place.

The following data indicate the results that can be expected, the degree of concordance and accuracy.

TABLE 1.

Results of experiments on a commercial phosphate-starch mixture to which varying amounts of arsenic trioxid were added before digestion.

SAMPLE DIGESTED	AMOUNT DIGESTED ORIGINAL SAMPLE USED IN TEST	TOTAL ARSENIC TRIOXID FOUND	ADDED ARSENIC TRIOXID IN TEST PORTION	AMOUNT ADDED ARSENIC TRIOXID RECOVERED[a]
grams	*grams*	*parts per million*	*parts per million*	*parts per million*
5.0	2.5	0.4	0.0	--
10.0	5.0	0.8	0.0	--
10.0	5.0	0.7	0.2	0.1
10.0	5.0	1.6	1.0	1.0
10.0	5.0	2.0	2.0	1.4
10.0	5.0	0.65	0.0	--
10.0	5.0	0.7	0.2	0.1
10.0	5.0	1.8	1.0	1.2
10.0	5.0	1.6	2.0	1.0
10.0	5.0	0.6	0.0	--
10.0	5.0	0.6	0.2	0.0
10.0	5.0	1.2	0.6	0.6
10.0	5.0	0.9	0.8	0.3
5.0	2.5	0.8	0.0	--
5.0	2.5	1.3	0.4	0.7
5.0	2.5	1.6	1.2	1.0
5.0	2.5	2.0	1.6	1.4
10.0	5.0	0.8	0.5	0.2
10.0	5.0	0.9	0.5	0.3
10.0	5.0	0.8	0.5	0.2
10.0	5.0	0.8	0.0	--
10.0	5.0	0.8	0.2	0.2
10.0	5.0	1.0	0.6	0.4
10.0	5.0	1.3	0.8	0.7
5.0	2.5	0.6	0.0	--
5.0	2.5	1.0	0.4	0.4
5.0	2.5	1.4	1.2	0.8
5.0	2.5	2.0	1.6	1.4
10.0[b]	5.0	0.5	0.0	--
10.0	5.0	1.4	0.2	0.8
10.0	5.0	0.9	0.4	0.3
10.0	5.0	1.1	0.6	0.5
10.0	5.0	0.4	0.0	--
10.0	5.0	0.5	0.0	--
10.0	5.0	0.8	0.1	0.2
10.0	5.0	0.9	0.2	0.3
10.0	5.0	1.1	0.3	0.5
10.0	5.0	0.8	0.4	0.2
10.0	5.0	1.0	0.5	0.4
10.0	5.0	1.5	0.6	0.9

[a] The phosphate-starch mixture was not arsenic-free. The average of 10 determinations made as above without arsenic addition was 0.6 part per million. This amount was subtracted from the total arsenic trioxid found to obtain the amount of added arsenic trioxid that was recovered.

[b] To each of the last 12 samples 0.5 gram of sodium chlorid was added.

Work was also carried out on the estimation of arsenic in gelatin, but the results do not justify a report at this time. The work is still in progress, as is that on a general hydrochloric acid distillation method which would be applicable to all foods.

Two recommendations adopted by the association in 1915 were:

"That the gravimetric and volumetric methods for tin, tested this year, be adopted by the association as provisional.

"That further study be made of other methods for the determination of tin."

For reasons indicated above, it was not possible to carry out the proposed work on these two recommendations. Work is now in progress on other methods for the determination of tin, especially a modification of Parry's method as used by Dr. W. B. D. Penniman.

RECOMMENDATIONS.

It is recomended—

(1) That the revised Gutzeit procedure and its application to baking materials be made the subject of collaborative work for the year 1917 with a view to its provisional adoption in 1917.

(2) That further study be made of the application of the method to gelatin and other food products.

(3) That the provisional gravimetric and volumetric methods for the determination of tin be subjected to further study with a view to final adoption in 1917.

(4) That further study be made of other methods for the determination of tin.

(5) That the methods for the determination of copper, zinc, nickel and aluminium in food products be made the subject of study by the association as soon as possible.

W. D. Collins (Bureau of Chemistry, Washington, D. C.) presented a paper on "C. R. Smith's Method for the Determination of Arsenic[1]".

The meeting adjourned at 5.07 p. m. for the day.

---

[1] *J. Ind. Eng. Chem.*, 1918, **10**: 360.

THIRD DAY.

WEDNESDAY—MORNING SESSION.

REPORT OF COMMITTEE A ON RECOMMENDATIONS OF REFEREES AND REVISION OF METHODS.

By W. W. SKINNER (Bureau of Chemistry, Washington, D. C.), *Chairman.*

[Phosphoric acid (basic slag, to cooperate with committee on vegetation tests on the availability of phosphoric acid in basic slag), nitrogen (special study of Kjeldahl method), potash, soils (nitrogenous compounds, lime requirements), inorganic plant constituents, insecticides and fungicides, and water.]

PHOSPHORIC ACID.

It is recommended—

(1) That the study of the preparation of neutral ammonium citrate solution, its use in determining reverted phosphoric acid and possible substitutes for it in this determination, be continued.

Approved.

(2) That in view of the conditions resulting from the European war, whereby the price of molybdic acid has been more than quadrupled and 100 per cent molybdic acid practically removed from the United States markets, the referee study the determination of phosphoric acid with a view to recommending an optional method not requiring the use of molybdic acid.

Approved.

(3) That the volumetric method, dissolving the slag in sulphuric and nitric acids[1], be adopted as an official method for total phosphoric acid in basic slag.

Approved.

(4) That this association instruct its referee on phosphoric acid to give prominent attention to the question of methods of determining available phosphoric acid in slags, the chemical ingredients influencing the same, and the bibliography on the subject.

Sufficient reports are already in the hands of your committee to be of service to the referee on phosphoric acid in his chemical investigations. It seems unnecessary to the committee to wait until all of the vegetation results are at hand before tentative methods of analysis are submitted to the association.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1917, 3: 90.

NITROGEN.

It is recommended—

(1) That the tentative ferrous-sulphate-zinc-soda method be adopted as official.

Approved.

(2) That, owing to the conflicting results on previous work, the use of glass wool in the neck of the distillation flask receive further study.

Approved.

(3) That further study be made of the effect of permanganate at the end of the digestion in the Kjeldahl modified method when used on a nitrate salt.

Approved.

(4) That the use of sodium sulphate in the Gunning method in place of potassium sulphate be tried out on a variety of organic substances of known origin, as well as of difficult oxidation.

Approved.

(5) That no further investigation of the Jones and Street methods for the determination of organic nitrogen activity be made.

Approved.

POTASH.

It is recommended—

(1) That the work on the availability of potash be continued.

Approved.

(2) That the referee next year study further the barium hydroxid process of the perchlorate method on mixed fertilizers of known potash content.

Approved.

(3) That the official method for the preparation of solution[1] be revised to read as follows:

Place 2.5 grams of the sample upon a 12.5 cm. filter paper and wash with successive portions of boiling water into a 250 cc. flask until the filtrate amounts to about 200 cc. Add to the hot solution a slight excess of ammonium hydroxid and sufficient ammonium oxalate to precipitate all of the lime present, cool, dilute to 250 cc., mix, and pass through a dry filter.

After a lengthy discussion, the proposed revision was disapproved by the association, and the matter referred to the referee for next year.

SOILS.

It is recommended—

(1) That further study be made of methods for total sulphur in soils, including a comparison of the following methods: Sodium peroxid fusion; heating soil with magnesium nitrate solution, as used for total phosphorus

[1] *Assoc. Official Agr. Chemists, Methods*, 1906, 12, **41** (a).

in soils; modification of Eschka's method for sulphur in coal; ignition of soil with mixtures of magnesium oxid, sodium carbonate and ammonium nitrate.

Approved.

(2) That methods for the determination of the total constituents of soils be studied with a view to substituting them for the "strong acid digestion"[1] and be referred to the referee for next year.

Approved.

(3) That the recommendation of the committee in 1915 that a modification of the Marr method be made a provisional method[2] be reconsidered, and that the adoption of a method for the determination of inorganic carbon in soils be held in abeyance, pending further investigation.

Approved.

INORGANIC PLANT CONSTITUENTS.

It is recommended—

(1) That the methods as outlined for calcium, magnesium, iron and aluminium[3] be further studied on solutions approximating the composition of the ash from cereals.

Approved.

(2) That the colorimetric method for the determination of manganese be further studied.

Approved.

INSECTICIDES AND FUNGICIDES.

It is recommended—

(1) That the method for the determination of arsenic trioxid in lead arsenate[4] be adopted as a tentative method.

Approved.

(2) That the method for the determination of arsenic pentoxid in lead arsenate[5] be adopted as a tentative method.

Approved.

(3) That further study be made of methods for the determination of copper, lead and zinc in such preparations as Bordeaux-lead arsenate, Bordeaux-zinc arsenite, etc.

Approved.

(4) That further comparison be made of the zinc chlorid and iodin methods in the analysis of lime sulphur solutions.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 22, **11**.
[2] *J. Assoc. Official Agr. Chemists*, 1917, 3: 60.
[3] *Ibid.*, 1920, 3: 329.
[4] *Ibid.*, 1920, 3: 332.
[5] *Ibid.*, 1920, 3: 363.

The foregoing recommendation, a substitute for the recommendation of the referee, resulted in considerable discussion, and a motion by Mr. Doolittle that the zinc chlorid method be made a tentative method and that the referee be directed to continue the study of the same, was duly seconded and carried.

(5) That cooperative work be done on the Gyory method for titrating As^{III} in hydrochloric acid solution with a solution of potassium bromate.

Approved.

(6) That Method I for total arsenic oxid[1] be dropped.

Approved.

(7) That the methods for the determination of moisture, free acetic acid and free ammonia proposed in 1910[2] and adopted as official (final action in 1912[3]) be dropped.

Approved.

(8) That all other methods for insecticides and fungicides be adopted as tentative and official methods, as given in the *Association of Official Agricultural Chemists, Methods*, 1916, **VII**, 63–77, except as further modified in the 1916 Report of the Referee on Insecticides[4].

Approved.

NOTE.—Mr. Skinner explained that the last above-mentioned recommendation was made for the purpose of covering certain points in the methods which have been slightly modified.

WATER.

It is recommended—

(1) That the following method for the determination of lithium, potassium and sodium be adopted in 1917 as an official method:

Dissolve the total alkali chlorids in a minimum amount of cold water in a tall 200 cc beaker (1.5 cc. will be more than sufficient for 0.5 gram of the salts). Add 1 drop of concentrated hydrochloric acid and gradually 20 cc. of absolute alcohol, dropping the alcohol into the center of the beaker (not on the sides) while rotating. Precipitate the sodium and potassium chlorid in a perfectly uniform granular condition. In a similar manner, while rotating the beaker, add 60 cc. of ether (sp. gr. 0.716–0.717) and allow the mixture to stand about 5 minutes, or until the precipitate is well agglomerated and the supernatant liquid almost clear. Occasionally rotate the beaker.

Filter the mixture through a weighed Gooch crucible into an Erlenmeyer flask, using a bell-jar arrangement. Thoroughly wash the beaker with a mixture of 1 part of alcohol and 4–5 parts of ether. A rubber-tipped rod is necessary for this purpose. Also thoroughly wash the precipitate in the Gooch crucible and set the crucible aside. Thoroughly wash the funnel to remove any lithium therefrom into the flask containing the filtrate.

Evaporate the filtrate to dryness on the steam bath (using a blast). Take up the residue with 10 cc. of absolute alcohol, warming if necessary, so that practically everything passes into solution. If a slight film remains on the bottom of the flask and sides, remove it by rubbing with a rubber-tipped glass rod. While rotating the flask,

[1] U. S. Bur. Chem. Bull. **107**, rev.: 28.
[2] *Ibid.*, **137**: 38.
[3] *Ibid.*, **162**: 49.
[4] *J. Assoc. Official Agr. Chemists*, 1920, **3**: 331.

add 50 cc. of ether (sp. gr. at 35°C., 0.716–0.717). Add 1 drop of concentrated hydrochloric acid, rotate the flask and allow to stand for 30 minutes. It is well to rotate the flask at frequent intervals. When the fine precipitate has agglomerated (only a very small amount is usually precipitated), filter it into a tall beaker through the same crucible as used in the first precipitation, a bell-jar arrangement being employed. Wash the residue with ether-alcohol mixture, using the same precautions as outlined in the first precipitation. After drying in an oven, gently ignite the crucible, cool, and weigh.

Evaporate the ether-alcohol solution of lithium on the steam bath. Take up the residue in a little water and add a slight excess of sulphuric acid. Carefully transfer the solution to a weighed porcelain or platinum dish. Evaporate the solution as far as possible on the same steam bath and gently ignite the residue over a flame. By placing the dish on a triangle over an asbestos gauze and using a low flame, the solution can be evaporated without spattering.

Then carefully ignite the residue over a full flame. When charring has occurred, it is well to repeat the ignition with sulphuric acid.

Calculate to lithium, using the factor 0.12625.

Remove the chlorid of sodium and potassium from the Gooch crucible with 25–50 cc. of hot water, collecting the filtrate in a porcelain dish by means of the bell-jar arrangement. Add sufficient platinic chlorid solution (containing the equivalent of 1 gram of metallic platinum, *i. e.*, 2.1 grams H_2PtCl_6 in every 10 cc.) to convert sodium and potassium to their respective double chlorids and evaporate to dryness. Treat the residue with 80% alcohol, filter, and wash until the excess of platinic chlorid and sodium platinic chlorid has been removed. Dry the filter and precipitate, dissolve the residue in hot water, and transfer to a weighed platinum dish. Evaporate on the steam bath, dry for 30 minutes in the oven at 100°C. and weigh as potassium platinic chlorid; calculate to potassium chlorid, using the factor 0.30673, and to potassium, using the factor 0.16085.

Find the weight of sodium chlorid by subtracting the weight of potassium chlorid from the total weight of the sodium chlorid and potassium chlorid obtained above. Calculate to sodium, using the factor 0.39343. Report as mg. sodium, mg. potassium, and mg. lithium per 50 cc. of solution.

Approved.

(2) At the suggestion of Mr. R. E. Doolittle of the Committee on Editing Methods of Analysis, certain methods have been recommended for adoption as official methods. These methods have been published in the *Association of Official Agricultural Chemists, Methods*, 1916, **IV**, but are not methods that have received recommendation for final adoption. In order to have the record straight, the referee recommends the adoption of the following methods as official:

(a) Method for turbidity, (a) and (b)[1].

(b) Method for color, **3** and **4**[1].

(c) Method for odor, **5**[1].

(d) The Schulze-Trommsdorf method for the determination of required oxygen, **22** and **23**[2].

(e) Method I and Method II for dissolved oxygen, **24**, **25**, **26** and **27**[3].

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 35.
[2] *Ibid.*, 39.
[3] *Ibid.*, 40.

(f) Method for the determination of specific gravity, **30**[1].

(g) Method for the determination of hydrogen sulphid, **37**[1].

(h) Method for temporary hardness, **70**[2].

(i) Method for alkalinity, **71**, **72**, **73** and **74**[2].

(j) Method for total hardness, **75** and **76**[3].

(k) Method for permanent or non-carbonate hardness, **77**[3].

Adopted as official.

(3) That the method for free carbon dioxid[4] remain a tentative method.

Approved.

(4) That the Gutzeit method for the determination of arsenic[5] be printed in the methods for the analysis of water as an optional official method.

After some discussion a motion to postpone action on this last recommendation for another year was carried.

REPORT OF COMMITTEE B ON RECOMMENDATIONS OF REFEREES AND REVISION OF METHODS.

By R. E. STALLINGS[6] (State Department of Agriculture, Atlanta, Ga.), *Chairman.*

[Foods and feeding stuffs (sugar, crude fiber, stock feed adulteration, organic and inorganic phosphorus, water), dairy products (separation of nitrogenous substances in milk and cheese), saccharine products (maple products, honey, sugar house products), drugs (medicinal plants, alkaloids, synthetic products, medicated soft drinks, balsams and gum resins, enzyms), testing of chemical reagents and micro-analytical methods.]

FOODS AND FEEDING STUFFS.

It is recommended—

(1) That a further study of sulphur dioxid in bleached grains be made by collaborators.

Approved.

(2) That the method for determining the acidity of corn, as described by Black and Alsberg[7], be considered by the referee next year with a view to its adoption as an official method, and that the method be studied to see if changes are necessary to make it applicable to grains other than corn.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 41.
[2] *Ibid.*, 50.
[3] *Ibid.*, 51.
[4] *Ibid.*, 42, **38**.
[5] *Ibid.*, 171.
[6] Since deceased.
[7] Bur. Plant Ind. Bull. 199.

SUGAR.

It is recommended—

(1) That the modifications proposed last year for determining sucrose by acid and invertase inversion be further studied.

Approved.

(2) That the work upon determining small amounts of reducing sugars in the presence of sucrose be continued.

Approved.

(3) That the methods of determining copper by reduction of the oxid in alcohol vapors be investigated.

Approved.

(4) That the optical methods for estimating raffinose in beet products be examined with special reference to hydrolysis by means of enzyms.

Approved.

(5) That details of mixing raw sugars be studied with a view to reducing moisture changes.

Approved.

(6) That the influence of temperature upon polarization by sugars other than sucrose be studied.

Approved.

(7) That recommendations 2, 3 and 5, made by W. D. Horne[1], be referred to the Committee on Editing Methods of Analysis.

Approved.

(8) That the referees continue in collaboration with the Bureau of Standards the preparation of a table of reduction factors for the more common reducing sugars.

Approved.

CRUDE FIBER.

It is recommended—

(1) That the one filtration method[2] be investigated further.

Approved.

(2) That the matter of a uniform filtering medium be studied further.

Approved.

STOCK FEED ADULTERATION.

It is recommended—

(1) That samples be sent out the coming year for cooperation in the determination of grit and weed seeds in scratch feeds.

Approved.

(2) That a key or outline for the qualitative detection of adulterants in feeding stuffs be prepared and submitted at the next meeting.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1919, **3**: 263.
[2] *Ibid.*, 256.

(3) That the following recommendations of 1914 be studied during the coming year:

(1) That methods for the detection of peat, dried at high temperatures, in feeding stuffs be investigated.

Approved.

(2) That the maximum percentage of foreign materials permissible in mill by-products be investigated.

Approved.

ORGANIC AND INORGANIC PHOSPHORUS.

It is recommended—

(1) That the magnesia mixture method[1] for the estimation of water-soluble inorganic phosphorus in flesh be adopted as an official method of this association, with one minor change of detail in the interest of economy of reagents, namely, that the amount of magnesia mixture used in extracts from 10 to 12 gram samples be reduced from 50 to 10 cc.

The committee feels that sufficient collaboration has not been reported and that final action should be deferred until further collaboration.

Final action postponed.

(2) That further work be done with the magnesia mixture method[1] on brain; that other glandular tissues be studied.

Approved.

WATER.

It is recommended—

(1) That the referee for the ensuing year study further methods for determining water in foods and feeding stuffs, especially the use of the vacuum method with calcium oxid for cereal products in comparison with the official methods.

Approved.

DAIRY PRODUCTS.

It is recommended—

(1) That further study be made on the Harding-Parkin method for fat determination[2] in comparison with the present official and provisional methods.

Approved.

(2) That further study be given to enzym reactions of milk.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1916, **1**: 562; 1919, **3**: 264.
[2] *J. Ind. Eng. Chem.*, 1913, **5**: 131.

SEPARATION OF NITROGENOUS SUBSTANCES.

It is recommended—

(1) That the referee for next year attempt to determine the relative amounts of some of the dissociation products in water-soluble and water-insoluble meat proteins.

Approved.

(2) That study be continued leading to the adoption of methods for the determination of the non-casein proteins and the products of protein decomposition in milk.

Approved.

SACCHARINE PRODUCTS.

No report or recommendations.

DRUGS.

It is recommended—

(1) That comparative work be resumed on the ricin method for the assay of pepsin[1] and that the methods outlined for the identification and essay of papain be studied cooperatively.

Approved.

(2) That the appointment of the referee on balsams be continued, and that a study be made of the methods of demonstrating the difference between the natural and the artificial product.

Approved.

(3) That the methods for the determination of strychnin in tablet triturates[2] be made provisional.

Approved.

(4) That the method for the determination of strychnin in liquids[2] where it occurs as the only alkaloid be made provisional.

Approved.

(5) That a further study be made of the method for determining atropin in tablets[3].

Approved.

(6) That the work on alkaloids be extended to a study of methods for the determination of strychnin and quinin in admixture.

Approved.

(7) That the work on mixtures containing synthetic products be continued.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 363.
[2] *J. Assoc. Official Agr. Chemists*, 1919, 3: 189; 1920, 3: 379.
[3] *Ibid.*, 1920, 3: 379.

TESTING OF CHEMICAL REAGENTS.

It is recommended—

(1) That the work on the determination of alcohol in pharmaceutical preparations be continued.

Approved.

(2) That the method for the determination of the strength of acetic anhydrid[1] be studied cooperatively.

Approved.

(3) That the work on tests for purity of immiscible organic solvents be taken up.

Approved.

MICRO-ANALYTICAL METHODS.

New subject.

REPORT OF COMMITTEE C ON RECOMMENDATIONS OF REFEREES AND REVISION OF METHODS.

By H. E. BARNARD[2] (State Board of Health, Indianapolis, Ind.), *Chairman.*

[Food preservatives, coloring matters in foods, metals in foods, fruit and fruit products, canned vegetables, cereal foods, wines, soft drinks (bottlers' products), distilled liquors, beers, vinegars, flavoring extracts, meat and meat products (separation of nitrogenous compounds in meat products, meat extracts), dairy products, edible fats and oils, spices and other condiments, cacao products, coffee, tea, baking powder.]

FOOD PRESERVATIVES.

It is recommended—

(1) That Method I, as given in the report of the referee on preservatives[3], for the determination of saccharin in the absence of other ether-soluble sulphur compounds be adopted as a tentative method to replace the method given in Bureau of Chemistry Bulletin 107 (Revised), page 183, and in the *Association of Official Agricultural Chemists, Methods*, 1916, 145.

Approved.

(2) That the Jorissen test for salicylic acid, as given in the report of the referee on preservatives[4], be adopted as a tentative method.

Approved.

(3) That further work be done on Method II, as given in the report of the referee on preservatives[5], for the determination of saccharin in

[1] Acetic anhydrid was treated in the cold with anilin, as described by Menschutkin and Vasilieff (*J. Russ. Phys. Chem. Soc.*, 1889, **21**: 190). The acetanilid formed was weighed.
[2] Present address, American Institute of Baking, Minneapolis, Minn.
[3] *J. Assoc. Official Agr. Chemists*, 1920, **3**: 504.
[4] *Ibid.*, 512.
[5] *Ibid.*, 505.

the presence of mustard oil; that other methods not dependent upon the sulphur component of saccharin be investigated; and that further work be done upon the determination of saccharin in baked flour preparations.

Approved.

(4) That the following methods be made official, the paragraph numbers and titles being given as they appear in the *Association of Official Agricultural Chemists, Methods*, 1916, 141–54:

SALICYLIC ACID.

1 PREPARATION OF SAMPLE.—OFFICIAL.

2 *Ferric Chlorid Test.—Qualitative.—Official.*

4 *Colorimetric Method.—Quantitative.—Official.*

BENZOIC ACID.

6, 7 PREPARATION OF SAMPLE.—OFFICIAL.

9 *Ferric Chlorid Test.—Qualitative.—Official.*

10 *Modified Mohler Test.—Qualitative.—Official.*

11 *Quantitative Method.—Official.*

SACCHARIN.

12 *Qualitative Test.—Official.*

BORIC ACID AND BORATES.

14 *Qualitative Test.—Official.*

15 *Quantitative Method.—Official.*

FORMALDEHYDE.

16 PREPARATION OF SAMPLE.—OFFICIAL.

17 *Phenylhydrazin Hydrochlorid Method.—Official.*

18 *Hehner Method.—Official.*

19 *Leach Method.—Official.*

20 *Phenylhydrazin Hydrochlorid and Sodium Nitro-prussid Test.—Official.*

21 *Phenylhydrazin Hydrochlorid and Potassium Ferricyanid Test.—Official.*

22 *Phenylhydrazin Hydrochlorid and Ferric Chlorid Test.—Official.*

23 *Phloroglucol Method.—Official.*

FLUORIDS.

24 *Method I.—Modified Method of Blarez.—Official.*

25 *Method II.—Official.*

SULPHUROUS ACID.

30 *Method I.—Distillation Method.—Official.*

31 *Method II.—Direct Titration Method.—Official.*

32 DETERMINATION OF FREE SULPHUROUS ACID.—OFFICIAL.

FORMIC ACID.

38, 39, 40 *Quantitative Method.—Official.*

Approved.

(5) That the other methods in this chapter remain tentative.

Approved.

COLORING MATTERS IN FOODS.

No recommendations.

METALS IN FOODS.

It is recommended—

(1) That the revised Gutzeit procedure and its application to baking materials be made the subject of collaborative work for the year 1917.

Approved.

(2) That further study be made of the application of the method to gelatin and other food products.

Approved.

(3) That the tentative gravimetric and volumetric methods for tin be subjected to further study.

Approved.

(4) That further study be made of other methods for the determination of tin.

Approved.

(5) That the methods for the determination of copper, zinc, nickel and aluminium in food products be made the subject of study.

Approved.

FRUIT AND FRUIT PRODUCTS.

It is recommended—

(1) That the methods for the determination of malic acid[1] be adopted as tentative methods.

Approved.

(2) That the method for the determination of citric acid[2] be adopted as a tentative method.

Approved.

CANNED VEGETABLES.

It is recommended—

That the Howard method as amended for the examination of tomato pulp and its products be retained as a tentative method. The method is as follows:

49 APPARATUS.

(a) *Compound microscope.*—Equipped with apochromatic objectives and compensating oculars, giving magnifications of approximately 90, 180, and 500 diameters. These magnifications can be obtained by the use of 16 and 8 mm. Zeiss apochromatic

[1] *J. Assoc. Official Agr. Chemists*, 1919, 3: 403–5.
[2] *Ibid.*, 405–6.

objectives with X6 and X18 Zeiss compensating oculars, or their equivalents, such as the Spencer 16 and 8 mm. apochromatic objectives with Spencer X10 and X20 compensating oculars, the drawtube of the microscope being adjusted as directed below.

(b) *Thoma-Zeiss blood counting cell.*

(c) *Howard mold counting cell.*—Constructed like a blood counting cell but with the inner disk (which need not be ruled) about 19 mm. in diameter.

50 MOLDS.—TENTATIVE.

Clean the special Howard cell so that Newton's rings are produced between the slide and the cover glass. Remove the cover and place, by means of a knife blade or scalpel, a small drop of the sample upon the central disk; spread the drop evenly over the disk and cover with the cover glass so as to give an even spread to the material. It is of the utmost importance that the drop be mixed thoroughly and spread evenly; otherwise the insoluble matter, and consequently the molds, are most abundant at the center of the drop. Squeezing out the more liquid portions around the margin must be avoided. In a satisfactory mount Newton's rings should be apparent when finally mounted and none of the liquid should be drawn across the moat and under the cover glass.

Place the slide under the microscope and examine with a magnification of about 90 diameters and with such adjustment that each field of view represents approximately 1.5 sq. mm. of area on the mount. This area is of vital importance and may be obtained by adjusting the drawtube to the proper length as determined by actual measurement of the field, a 16 mm. Zeiss apochromatic objective with a Zeiss X6 compensating ocular or a Spencer 16 mm. apochromatic objective with a Spencer X10 compensating ocular, or their equivalents, being used to obtain the proper magnification.

Observe each field as to the presence or absence of mold filaments and note the result as positive or negative. Examine at least 50 fields, prepared from two or more mounts. No field should be considered positive unless the aggregate length of the filaments present exceeds approximately one-sixth the diameter of the field. Calculate the proportion of positive fields from the results of the examination of all the observed fields and report as percentage of fields containing mold filaments.

51 YEASTS AND SPORES.—TENTATIVE.

Fill a graduated cylinder with water to the 20 cc. mark, and then add the sample till the level of the mixture reaches the 30 cc. mark. Close the graduate, or pour the contents into an Erlenmeyer flask, and shake the mixture vigorously 15–20 seconds. To facilitate thorough mixing, the mixture should not fill more than three-fourths of the container in which the shaking is performed. For tomato sauce or pastes, or products running very high in the number of organisms, or of heavy consistency, 80 cc. of water should be used with 10 cc. or 10 grams of the sample. In the case of exceptionally thick or dry pastes, it may be necessary to make an even greater dilution.

Pour the mixture into a beaker. Thoroughly clean the Thoma-Zeiss counting cell so as to give good Newton's rings. Stir thoroughly the contents of the beaker with a scalpel or knife blade, and then, after allowing to stand 3–5 seconds, remove a small drop and place upon the central disk of the Thoma-Zeiss counting cell and cover immediately with the cover glass, observing the same precautions in mounting the sample as given under **50**. Allow the slide to stand not less than 10 minutes before beginning to make the count. Make the count with a magnification of about 180. to obtain which the following combinations, or their equivalents, should be employed: 8 mm. Zeiss apochromatic objective with X6 Zeiss compensating ocular, or an 8 mm.

Spencer apochromatic objective with X10 Spencer compensating ocular with drawtube not extended.

Count the number of yeasts and spores on one-half of the ruled squares on the disk (this amounts to counting the number in eight of the blocks, each of which contains twenty-five of the small ruled squares). The total number thus obtained equals the number of organisms in $\frac{1}{60}$ cmm. if a dilution of 1 part of the sample with 2 parts of water is used. If a dilution of 1 part of the sample with 8 parts of water is used, the number must be multiplied by 3. In making the counts, the analyst should avoid counting an organism twice when it rests on a boundary line between two adjacent squares.

52 BACTERIA.—TENTATIVE.

Estimate the bacteria from the mounted sample used in **51**, but allow the sample to stand not less than 15 minutes after mounting before counting. Employ a magnification of about 500, which may be obtained by the use of an 8 mm. Zeiss apochromatic objective with an X18 Zeiss compensating ocular with drawtube not extended, or an 8 mm. Spencer apochromatic objective with an X20 Spencer compensating ocular having a tube length of 190, or their equivalents. Count and record the number of bacteria in a small area consisting of five of the small-sized squares. Move the slide to another portion of the field and count the number on another similar area. Count five such areas, preferably one from near each corner of the ruled portion of the slide and one from near the center. Determine the average number of bacteria per area and multiply by 2,400,000, which gives the number of bacteria per cc. If a dilution of 1 part of the sample with 8 parts of water, instead of 1 part of the sample with 2 parts of water, is used in making up the sample, then the total count obtained as above must be multiplied by 7,200,000. Omit the micrococci type of bacteria in making the count.

Approved.

CEREAL FOODS.

It is recommended—

That the following methods be studied during the coming year:

(1) *Moisture.*—Comparison of the official method with the vacuum method, using calcium oxid.

(2) *Gluten.*—Comparison of methods of washing gluten by using (a) distilled water; (b) water containing sodium chlorid; (c) ordinary hydrant water.

(3) *Soluble carbohydrates.*—Comparison of methods using different strengths of hydrochloric acid.

(4) *Cold water extract.*

(5) *Chlorin.*

Approved.

WINES.

It is recommended—

(1) That the method suggested by the associate referee for 1915[1] for determining the acidity in wines, and discussed by the referee for 1916[2], be adopted as tentative.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1917, **2**: 186.
[2] *Ibid.*, 1920, **3**: 409.

(2) That the following methods be studied during the coming year:

(a) Determination of tartaric acid present as esters by saponifying before determining the total tartaric acid.

(b) Determination of the acidity of red wines by the clarification method[1].

(c) Determination of glycerol according to the Rothenfusser method[2].

Approved.

SOFT DRINKS.

New subject. No report.

DISTILLED LIQUORS.

No recommendations.

BEERS.

No recommendations.

VINEGARS.

No recommendations.

FLAVORING EXTRACTS.

It is recommended—

(1) That the methods of analysis for imitation vanilla preparations containing large quantities of vanillin and coumarin be given further study.

Approved.

(2) That the advisability of making a preliminary test for coumarin in vanilla extracts be studied.

Approved.

(3) That the value of the test for the detection of vanilla resins be studied.

Approved.

(4) That the applicability of Hortvet and West's method for determining alcohol in lemon and orange extracts be studied.

Approved.

(5) That Mitchell's polarization method be studied for the purpose of determining the most desirable factors to be used, especially with reference to the natural variation in the oils and the influence of dilution.

Approved.

(6) That Albright's details of the Kleber method for citral in lemon and orange oil[3] be studied.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1920, **3**: 410.
[2] *Z. Nahr. Genussm.*, 1912, **23**: 332–7.
[3] *J. Assoc. Official Agr. Chemists*, 1920, **3**: 417.

(7) That available and new methods for determining benzoic acid in almond extract be studied.

Approved.

(8) That Howard's method[1] and the present tentative method of determining the oil in cassia, coumarin and clove extracts be further studied.

Approved.

MEAT AND MEAT PRODUCTS.

No report.

DAIRY PRODUCTS.

It is recommended—

(1) That the modifications of the Roese-Gottlieb method applied to plain ice cream, dried milk and malted milk be further studied.

Approved.

(2) That the Schmidt-Bondzynski modified method for the determination of fat in cheese be adopted as a tentative method, and further studied.

Approved.

(3) That Patrick's method for the determination of sucrose in sweetened condensed milk, as outlined below, be adopted as a tentative method:

PATEIN AND DUFAU'S REAGENT[2].

To 220 grams of yellow mercuric oxid and 300–400 cc. of water in an evaporating dish, add cautiously sufficient concentrated nitric acid (about 140 cc.) just to dissolve the mercuric oxid, then add a solution of sodium hydroxid in sufficient quantity to give a slight permanent precipitate, dilute to 1 liter and filter. (As this reagent tends to become more acid with age, through the deposition of basic salts of mercury, it should receive the addition of a little alkali from time to time.)

DETERMINATION.

To 50 grams of the 20 per cent solution, or 25 grams of a 40 per cent solution, of the sample in a 100 cc. graduated flask, add 25 cc. of water, then 5 cc. of the Patein and Dufau reagent, and shake well. Without delay run in, with constant shaking, sufficient N/2 sodium hydroxid to make the mixture practically neutral, but not alkaline, to litmus paper (12 to 13 cc. of N/2 sodium hydroxid is usually required; the amount should be determined beforehand on 5 cc. of the Patein and Dufau reagent). Make up to the mark with water, shake well, filter, and polarize in a 200 mm. tube at 20°C.

Invert the sucrose in 50 cc. of this solution by adding 5 cc. of concentrated hydrochloric acid and letting stand overnight at room temperature (above 20°C.). Obtain the invert reading at 20°C. without neutralizing the acid and multiply by 1.1 to correct for dilution.

---

[1] *J. Ind. Eng. Chem.*, 1911, 3: 252.
[2] *Ann. chim. anal.*, 1902, 7: 128; *Z. Nahr. Genussm.*, 1902, 5: 726.

A correction of the direct reading, and a further correction of the invert reading, for the volume occupied by the fat and proteins, using the factor 1.075 for fat and 0.80 for protein, should be made. After making these corrections, calculate the sucrose by the Clerget formula:

$$S = \frac{100\ (P - I)}{142.35 - \frac{T}{2}}$$ in which

S = per cent of sucrose;
P = direct reading in degrees Ventzke;
I = invert reading;
T = temperature at which polarization was made.

Approved.

EDIBLE FATS AND OILS.

It is recommended—

(1) That the method reported by the referee[1], for the detection of beef fat in lard by crystallization from acetone and the preparation and determination of the melting point of the fatty acids, be further studied with a view to its adoption as a tentative method in 1917.

Approved.

(2) That the potassium-salt-acetone method[2] for the separation of solid and liquid fatty acids be given further study.

Approved.

SPICES AND OTHER CONDIMENTS.

It is recommended—

(1) That the modification of the distillation method for water in whole spices, as reported by the associate referee, be given further study with particular reference to the size and dimensions of the apparatu and length of time of heating.

(2) That the subject of sampling and grinding and the preparation for analysis of each spice be studied.

COCOA AND COCOA PRODUCTS.

It is recommended—

(1) That the name of this subject be changed from "Cocoa and Cocoa Products" to "Cacao Products".

Approved.

(2) That the corrected formula for the polariscopic determination of sucrose and lactose be adopted as tentative.

Approved.

---

[1] *J. Assoc. Official Agr. Chemists*, 1920, 3: 433.
[2] *Ibid.*, 435.

(3) That the tentative method for the determination of fat[1] be changed to provide for a 4-hour extraction.

Approved.

(4) That the proposed modification of the Baier and Neumann method be further studied.

Approved.

(5) That the determination of the critical temperature of dissolution for the examination of cacao butter be further studied with a view to its adoption as a tentative method.

Approved.

(6) That the associate referee's test for tallow and hydrogenated oils be further studied.

Approved.

TEA AND COFFEE.

It is recommended—

That the Stahlschmidt method for caffein be further studied with a view to its adoption as an official method.

Approved.

BAKING POWDER.

It is recommended—

(1) That the Exner method for the gravimetric determination of lead (now a tentative method) be dropped, and that no further study of it be made.

Approved.

(2) That a further study be made of the Wichmann method and modifications for its improvement.

Approved.

(3) That a study be made of Bryan's modification of the Corper method for the electrolytic determination of lead in baking powder.

Approved.

(4) That a study be made of Chittick's method for the determination of lead.

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods*, 1916, 328.

REPORT OF COMMITTEE ON EDITING METHODS OF ANALYSIS[1].

Your Committee on Editing Methods of Analysis submitted at the meeting of the association last year a tentative draft of the revised methods. This draft was submitted in order that the members of the association might have an opportunity to study the changes made by the addition of new methods, deletion of obsolete and incorrect methods, rearrangements, changes in phraseology, etc. As a result, many voluntary criticisms and suggestions were received. The revised methods were also submitted to some of the members who were particularly familiar with their history, development and adaptability, in order to insure their correctness. As a result of the information thus secured, a considerable number of changes were introduced and the revised methods forwarded to the secretary of the association for publication. Errors, however, have slipped into the published methods due to oversight on the part of the committee and through editorial changes introduced into the text without participation on the part of the committee, which have necessitated a careful review of the methods as printed in the *Association of Official Agricultural Chemists, Methods*, 1916. The report as offered this year includes many more alterations than the committee would desire, but in fairness to the association it seems necessary that we should offer them for your consideration in a complete form.

The committee desires to make the following general recommendations:

(1) That the following listed general reference tables be placed by themselves in a separate chapter at the end of the methods and designated as Chapter XXX, and that appropriate changes be made in the marginal numbers and in the cross references to them in the text of the methods:

1 Munson and Walker's Table[2]. For calculating dextrose, invert sugar alone, invert sugar in the presence of sucrose, etc.

2 Kröber's Table[3]. For determining pentoses and pentosans.

3 Table for the densities of solutions of cane sugar at 20°C.[4]

4 Table of temperature corrections for changing percentages of sugar by specific gravity to true values at 20°C.[5]

5 Geerlig's Table[6]. For dry substances in sugar-house products by the Abbé refractometer, at 28°C.

6 Table of corrections for temperature to be used in conjunction with Table No. 5[7].

---

[1] Presented by R. E. Doolittle.
[2] *Assoc. Official Agr. Chemists, Methods*, 1916, 88–96.
[3] *Ibid.*, 112–7.
[4] *Ibid.*, 125–6.
[5] U. S. Bur. Standards Circ. **19**: 1916, 25.
[6] *Assoc. Official Agr. Chemists, Methods*, 1916, 127
[7] *Ibid.*, 128.

7 Alcohol Table[1]. For calculating the percentages of alcohol in mixtures of ethyl alcohol and water from their specific gravities.

8 Alcohol Table[2]. For calculating the percentages of alcohol in mixtures of ethyl alcohol and water from their Zeiss immersion refractometer readings at 17.5–25°C.

9 Table of international atomic weights, 1916.

Approved.

(2) That the word "chlorin" wherever it appears in the expressions "washed free from chlorin" and "washed practically free from chlorin" be changed to "chlorids".

Approved.

(3) That the gravimetric factors be restored throughout the text of the book of methods.

Approved.

At this point a motion was made, seconded and adopted that the By-laws be suspended.

(4) That, where the strength of solutions is given in terms of per cent, specific instructions be substituted giving the manner in which the solutions are to be prepared.

Approved.

(5) That all alkaloids be spelled with the final "e".

After considerable discussion a substitute motion was introduced recommending that alkaloids be spelled without the final "e". The substitute motion was duly seconded and adopted.

The committee desires to make the following specific recommendations:

I. FERTILIZERS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 1–15, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of fertilizers:

CHANGES.

(1) **5**, PREPARATION OF SOLUTION.

Combine the first and the last paragraphs and change to read as follows: "Treat 2 grams of the sample by one of the methods given below. In the case of (**d**) 2.5 grams may be used. Cool, dilute to 200 cc., or to 250 cc. if a 2.5 gram sample was used. Mix, and pour on a dry filter."

Approved.

---

[1] *Assoc. Official Agr. Chemists, Methods* 1916, 194–207.
[2] *Ibid.*, 208–35.

(2) **6**, DETERMINATION.

Line 5.—Eliminate "60–80" and substitute therefor "50", making the sentence read: "To the hot solution add 50 cc. of the molybdate solution for every decigram of phosphoric acid (P_2O_5) that is present."

Disapproved.

Mr. F. P. Veitch (Bureau of Chemistry, Washington, D. C.) made a motion that "70" be substituted for "60–80", making the sentence read: "To the hot solution add 70 cc. of the molybdate solution for every decigram of phosphoric acid (P_2O_5) that is present."

Approved.

Line 12.—Eliminate the words "add magnesia mixture".

Approved.

Line 13.—After "vigorously" insert "15 cc. of magnesia mixture for each decigram of phosphoric acid (P_2O_5) present," making the corrected sentence read: "Nearly neutralize with hydrochloric acid, cool, and from a burette add slowly (about 1 drop per second), stirring vigorously, 15 cc. of magnesia mixture for each decigram of phosphoric acid (P_2O_5) present."

Approved.

Line 16.—Eliminate the remainder of the paragraph beginning with the words "dry the filter" and substitute therefor the words "ignite to whiteness or to a grayish white, weigh and calculate to phosphoric acid (P_2O_5).", making the latter part of the paragraph read: "Let stand till the supernatant liquid is clear (2 hours is usually enough), filter, wash with the dilute ammonium hydroxid until the washings are practically free from chlorids, ignite to whiteness or to a grayish white, weigh and calculate to phosphoric acid (P_2O_5)."

Approved.

(3) **9**, DETERMINATION.

Line 14.—Change the word "a" before the word "beaker" to "the", making the sentence read: "Transfer the precipitate and filter to the beaker or precipitating vessel,".

Approved.

(4) **11**, *Volumetric Method.—Official.*

Line 2.—Eliminate the words "and ammonium hydroxid until a slight permanent precipitate is formed" and substitute therefor "nearly neutralize with ammonium hydroxid", making the sentence read: "add 10 cc. of concentrated nitric acid, nearly neutralize with ammonium hydroxid, dilute to 60 cc., and proceed as directed under **9**."

Approved.

(5) **12**, REAGENTS.

Line 5.—Eliminate the words "litmus or azolitmin paper" and substitute therefor "a saturated alcoholic solution of corallin", making the parenthetical expression read, "(testing with a saturated alcoholic solution of corallin)".

Approved.

(6) **13**, DETERMINATION.

Line 2.—Eliminate the word "Erlenmeyer", making the sentence read: "Heat 100 cc. of strictly neutral ammonium citrate solution (sp. gr. 1.09) to 65°C. in a 250 cc. flask placed in a warm water bath,".

Approved.

(7) **21**, DETERMINATION.

Line 7.—Eliminate the words "Do not add either potassium permanganate or potassium sulphid. Cool, dilute, neutralize, distil, and titrate with the standard alkali. In neutralizing", and substitute therefor "Complete the determination, as directed under **18**, except that neither potassium permanganate nor potassium sulphid is added. In making alkaline", making the sentences read: "Digest for a time after the mixture is colorless or nearly so, or until oxidation is complete. Complete the determination, as directed under **18**, except that neither potassium permanganate nor potassium sulphid is added. In making alkaline before distilling, it is convenient to add a few drops of phenolphthalein indicator, etc."

Approved.

(8) **27**, REAGENTS AND APPARATUS.

Line 1.—Insert the word "apparatus" after the word "the", making the sentence read: "The apparatus, reagents and standard solutions are described under **16**, **17**, **19** and **24**."

Approved.

(9) **32**, *Magnesium Oxid Method.—Official.*

At the end of the paragraph add the words "using cochineal or methyl red solution as indicator", making the sentence read: "and titrate with standard alkali solution, using cochineal or methyl red solution as indicator."

(10) **34**, *Zinc-Iron Method.—Official.*

At the end of the paragraph add the words "using cochineal or methyl red solution as indicator", making the sentence read: "Continue the distillation until 100 cc. have been distilled and titrate with standard alkali solution, using cochineal or methyl red solution as indicator."

(11) **35**, *Ferrous Sulphate-Zinc-Soda Method.—Tentative.*

At the end of the paragraph add the words "using cochineal or methyl red solution as indicator", making the sentence read: "and titrate with standard alkali solution, using cochineal or methyl red solution as indicator."

Recommendations 9, 10 and 11 approved.

(12) **38**, PREPARATION OF SAMPLE.

Line above this heading.—Eliminate the parenthetical expression "(Not applicable to fertilizers containing cottonseed meal or castor pomace.)".

Approved.

(13) **39**, DETERMINATION.

Line 2.—Before the word "Kjeldahl" insert the word "round-bottomed".

Approved.

(14) **40** (c), *80% alcohol.*

Eliminate the paragraph as printed and subsitute therefor the following:

"(c) *80% alcohol.*—Sp. gr. 0.8593 at $\frac{20^\circ \text{ C.}}{4^\circ}$."

Approved.

Attention was called to the fact that if each change made by the committee were to be passed upon separately it would take several days to dispose of the report of the committee. It was then decided that Mr. Doolittle should bring only questions involving actual changes in the methods to the attention of the association.

(15) **41** (a), *Mixed fertilizers.*

Line 2.—After the word "with" insert "successive small portions of", making the sentence read: "and wash with successive small portions of boiling water".

(16) **41** (c), *Organic compounds.*

Line 3.—Change "250" to "500".

Line 4.—Eliminate the words "and proceed as in (a)" and substitute therefor the words "cool, dilute to 500 cc., mix, pass through a dry filter and proceed as in **42** (a)", making the last sentence of this paragraph read : "Add a little strong hydrochloric acid, warm slightly in order to loosen the mass from the dish, transfer to a 500 cc. graduated flask, add ammonium hydroxid and ammonium oxalate, cool, dilute to 500 cc., mix, pass through a dry filter and proceed as in **42** (a)."

(17) Add a new paragraph after **41** (c) for the preparation of the solution of wood ashes, cotton hull ashes and similar materials, as follows:

"(d) *Ashes from wood, cotton hulls, etc.*—Boil 10 grams of the sample with 300 cc. of water for 30 minutes, add a slight excess of ammonium hydroxid to the hot solution and then sufficient ammonium oxalate to precipitate all of the lime present. Cool, dilute to 500 cc., mix, pass through a dry filter and proceed as in **42** (a)."

(18) **42** (d), *Water-soluble potash in wood ashes and cotton hull ashes.*

Line 1.—Change this title to agree with **41** (d), viz.: "(d) *Water-soluble potash in ashes from wood, cotton hulls, etc.*"

Line 2.—Change "(a)" after "**41**" to "(d)", making the reference read "**41** (d)".

(19) Between **42** (d) and Method II, Official, insert the following paragraph: "For the conversion of potassium platinic chlorid to potassium chlorid use the factor 0.3067; to potassium sulphate 0.3585; to potassium oxid 0.1938."

(20) **48**, PREPARATION OF SOLUTION.

Line 1.—Change "(e)" to "(g)", making the reference read "**5** (g)".

(21) **50**, *Volumetric Method.*

Line 1.—Change "(e)" to "(g)", making the reference read "**5** (g)".

Methods on fertilizers, as changed, adopted as a whole.

II. SOILS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 17–28, be changed as follows, and as changed

be adopted as the official and tentative methods of the association for the analysis of soils:

CHANGES.

(1) **2**, PREPARATION OF SAMPLE.—OFFICIAL.

Line 1.—Insert "(a)" at the beginning of the first paragraph.

Line 2.—Eliminate the words "to avoid" and substitute therefor the words, "and avoiding", making the sentence read: "After air-drying and weighing the sample, pulverize in a porcelain mortar, using a rubber-tipped pestle and avoiding the reduction of rock fragments, and pass through a sieve with circular openings $\frac{1}{25}$ inch (1 mm.) in diameter".

Line 6.—Insert "(b)" at the beginning of the second paragraph.

Line 6.—Eliminate the word "quantitative" and after the word "determination" insert the words "of the total quantity", making the paragraph read:

"(b) For the determination of the total quantity of any of the constituents, etc."

(2) Change the reference number "2" appearing in line 1 of paragraphs **3**, **6**, **9**, **10**, **11** and **28** to "**2** (a)".

(3) Change the reference number "2" in **23**, line 1, and **24**, line 2, to "**2** (b)", and insert the reference "**2** (b)" after the word "soil" in **25**, line 2.

(4) **5** (b), FIG. 2, PARR'S APPARATUS FOR THE DETERMINATION OF CARBON DIOXID.

Insert the letter "B" to designate the gas burette.

(5) **8**, APPARATUS.

Line 7.—After the word "tube" insert "of the same diameter", making the sentence read: "which in turn is furnished with a side tube of the same diameter extending through the condenser jacket (D)".

(6) **9**, DETERMINATION.

Line 11.—Eliminate the words "and most of the lower large bulb".

(7) **12**, INSOLUBLE RESIDUE.—OFFICIAL.

Last line of paragraph.—Eliminate "(a)" and substitute therefor the words, "beginning with 'Wash the residue from the filter'", making the sentence read: "and complete the determination as directed under **III**, **4**, beginning with 'Wash the residue from the filter' ".

(8) **13**, IRON, ALUMINIUM AND PHOSPHORIC ACID, COLLECTIVELY.—OFFICIAL.

Line 14.—Eliminate the word "filtrate" and substitute therefor the words "combined filtrates", making the sentence read: "Designate the combined filtrates as B".

(9) **14**, MANGANESE.—OFFICIAL.

Line 3.—Eliminate the second "of" and the preceding comma and substitute therefor the word "and", making the sentence read: "repeat the addition of bromin water and ammonium hydroxid and boil again."

(10) **16**, MAGNESIUM.—OFFICIAL.

Line 10.—After the expression "[**I**, **4** (**d**)]" eliminate the rest of the paragraph and substitute therefor the words: "dry, burn first at a moderate heat, then ignite intensely and weigh as magnesium pyrophosphate ($Mg_2P_2O_7$), and calculate to magnesium oxid (MgO)."

(11) **18 (a)**, *Standard sodium or potassium hydroxid solution.*

Line 1.—After "solution.—" insert the clause, "Prepare a solution of such strength that 100 cc. exactly neutralizes 16.19 cc. of normal acid;" and eliminate the words "strength such that", making the sentence read: "Prepare a solution of such strength that 100 cc. exactly neutralizes 16.19 cc. of normal acid; 1 cc. of this solution is equivalent to 0.0005 gram of phosphorus pentoxid (P_2O_5)."

(12) **23**, *Magnesium Nitrate Method.—Official.*

Line above this heading.—Change the title "Total Phosphorus" to "Total Phosphoric Acid."

(13) **25**, TOTAL POTASSIUM.—OFFICIAL.

Line 25.—Eliminate the words "by means of suction" and after "wash" insert "entirely free of soluble platinic salts", making the sentence read: "Filter through a small filter, wash entirely free of soluble platinic salts with 80% alcohol, then with ammonium chlorid solution [**I, 40 (a)**], and finally with 80% alcohol."

Line 26.—Eliminate the sentence reading: "Dry the precipitate on the filter and wash the precipitate with hot water into a weighed platinum dish, using suction." and substitute therefor the following: "Dry the precipitate on the filter, then dissolve and wash the precipitate through the filter with hot water into a weighed platinum dish."

(14) **27**, PHOSPHORUS SOLUBLE IN N/5 NITRIC ACID.—TENTATIVE.

Change the title "Phosphorus Soluble in N/5 Nitric Acid.—Tentative" to "Phosphoric Acid Soluble in N/5 Nitric Acid.—Tentative."

(15) **28**, CALCIUM CARBONATE REQUIRED.—TENTATIVE.

Line 6.—Change "0.001" to "0.01", and after the word "used" insert "assuming that the total amount of acid present is 2.5 times the amount in the solution titrated", making the parenthetical phrase read: "(0.01% on basis of the weight of soil used, assuming that the total amount of acid present is 2.5 times the amount in the solution titrated)".

(16) **29**, STATEMENT OF RESULTS.—OFFICIAL.

Transpose the line reading "Organic carbon" to a position immediately below "Volatile matter".

Change the line reading "Inorganic carbon" to "Carbon dioxid (CO_2) equivalent of inorganic carbon." After the words "Volatile matter" insert "other than carbon dioxid". Lines 18 and 20, change the word "phosphorus" to "phosphoric acid". This will change the column after the line reading "Sulphur trioxid (SO_3)" to read:

"Carbon dioxid (CO_2) equivalent of inorganic carbon.....
Volatile matter other than carbon dioxid.....
Organic carbon.....
Total nitrogen.....
Total phosphoric acid.....
Total potassium.....
Phosphoric acid soluble in N/5 nitric acid.....
Calcium carbonate required.....
Total....."

Methods on soils, as changed, adopted as a whole.

III. PLANT CONSTITUENTS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 29–33, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of inorganic plant constituents:

CHANGES.

(1) **III. PLANT CONSTITUENTS.**

Insert "Inorganic" before "Plant", making the title read, "Inorganic Plant Constituents."

(2) **8**, *Method II.—Tentative.*

Line 2.—After "**15**" insert the words "except that the solution is not to be concentrated", making the sentence read: "and proceed as directed under **II, 15**, except that the solution is not to be concentrated."

(3) **13**, CHLORIN.—OFFICIAL.

Eliminate the heading and the entire paragraph and substitute therefor the following:

CHLORIN.

13 *Gravimetric Method.—Official.*

Dissolve a weighed portion of the ash, prepared under **2**, in dilute nitric acid (1 to 10), filter, wash with hot water, and determine chlorin in the combined filtrate and washings as directed under **I, 16** (a).

(4) **14**, REAGENTS.

Line above this heading.—After the words "Volhard Method" insert the word "Official", making the line read "Volhard Method.—Official".

(5) **16**, POTASSIUM IN PLANTS.—OFFICIAL.

Line 1.—Change the cross reference "**I, 42**" to read "**I, 41** (c)".

Methods on inorganic plant constituents, as changed, adopted as a whole.

Mr. W. W. Skinner (Bureau of Chemistry, Washington, D. C.) made a motion that throughout the methods when a reference is made to a method under "Soils" it be changed to a method under "Waters".

Approved.

IV. WATERS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 35–52, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of waters:

CHANGES.

(1) **3** (a), *Standard color solution.*

Line 2.—After the formula "($PtCl_4.2KCl$)" insert "containing 0.5 gram of platinum".

Line 2.—After the formula "($CoCl_2.6H_2O$)" insert "containing 0.25 gram of cobalt", making the paragraph read: "Dissolve 1.246 grams of potassium platinic chlorid ($PtCl_4.2KCl$) containing 0.5 gram of platinum and 1 gram of crystallized cobalt chlorid ($CoCl_2.6H_2O$) containing 0.25 gram of cobalt in a small quantity of water, etc."

(2) **10** (d), *Nessler reagent.*

Line 3.—Eliminate the words "50% solution of potassium hydroxid" and substitute therefor the words "a solution containing 200 grams of potassium hydroxid", making the sentence read: "Add 400 cc. of a solution containing 200 grams of potassium hy, droxid (or an equivalent quantity of sodium hydroxid), dilute to 1 liter, allow to settle- and decant."

(3) **21**, DETERMINATION.

Line 10.—Eliminate the words "digesting at room temperature for 3 minutes" and substitute therefor the words "except that the digestion shall be at room temperature and for a period of 3 minutes", making the sentence read: "Correct for sulphids, nitrites and ferrous salts, if present, by subtracting the number of cc. of the standard permanganate absorbed by another 200 cc. portion of the sample when treated as above, except that the digestion shall be at room temperature and for a period of 3 minutes."

(4) **22** (a), *50% sodium hydroxid solution.*

Eliminate "50%" and add at the end of this line the sentence: "Dissolve 50 grams of sodium hydroxid in water, cool, and make to 100 cc.", making the paragraph read: "(a) *Sodium hydroxid solution.*—Dissolve 50 grams of sodium hydroxid in water, cool, and dilute to 100 cc."

(5) **27** (b), *2% potassium oxalate solution.*

Eliminate "2%" and add at the end of this line the sentence: "Dissolve 2 grams of potassium oxalate in 100 cc. of water.", making the paragraph read: "(b) *Potassium oxalate solution.*—Dissolve 2 grams of potassium oxalate in 100 cc. of water."

(6) **42**, *Colorimetric Method.*

At the end of the line insert the word "Official", making this line read, "Colorimetric Method.—Official."

(7) **43**, *Volumetric Method.*

At the end of the line insert the word "Official", making this line read, "Volumetric Method.—Official."

(8) **49**, SODIUM, POTASSIUM AND LITHIUM.—OFFICIAL.

Sixth paragraph, line 3.—Change "filtrates" to filtrate".

(9) **53** (b), *0.2% silver nitrate solution.*

Eliminate "0.2%" and add at the end of this line, "Dissolve 2 grams of silver nitrate in 1 liter of water.", making the paragraph read: "(b) *Silver nitrate solution.*—Dissolve 2 grams of silver nitrate in 1 liter of water."

(10) **55** (**a**), *10% sodium hydroxid solution.*

Eliminate "10%" and add at the end of this line the sentence: "Dissolve 10 grams of sodium hydroxid in water, cool and dilute to 100 cc.", making the paragraph read: "(**a**) *Sodium hydroxid solution.*—Dissolve 10 grams of sodium hydroxid in water, cool and dilute to 100 cc."

(11) **55** (**c**), *2% potassium or sodium nitrite solution.*

Eliminate "2%" and add at the end of this line the sentence: "Dissolve 2 grams of potassium or sodium nitrite in 100 cc. of water", making the paragraph read: "(**c**) *Potassium or sodium nitrite solution.*—Dissolve 2 grams of potassium or sodium nitrite in 100 cc. of water."

(12) **56**, DETERMINATION.

Line 18.—After the word "above" insert "beginning with 'Acidify with sulphuric acid' ", making the sentence read: "Prepare these standard tubes by treating measured quantities of a solution of known potassium iodid content, as described above, beginning with 'Acidify with sulphuric acid'."

(13) BIBLIOGRAPHY.

Reference 3.—Change "1912" to "1913", making that reference read: "Standard Methods of Water Analysis. Am. Pub. H. Assoc., 2nd ed., 1913, pp. 61 and 62."

Reference 7.—Change "1912" to "1913", making the last reference read: "Standard Methods of Water Analysis. Am. Pub. H. Assoc., 2nd ed., 1913, pp. 36 and 37."

Methods on water, as changed, adopted as a whole.

V. TANNING MATERIALS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Journal of the Association of Official Agricultural Chemists, Methods*, 1916, 53–7, be changed as follows, and as changed be adopted as the tentative methods of the association for the analysis of tanning materials:

CHANGES.

(1) **1** (**a**), *Solid extracts.*

Line 6.—Eliminate the last sentence of the paragraph and substitute therefor the sentence: "Allow to cool overnight at a temperature not below 19°C., bring to 20°C. by placing the flask in water, the temperature of which is not below 19°C., and make up to 1 liter."

(2) **1** (**b**), *Fluid extracts.*

Line 3.—Eliminate the last sentence of the paragraph and substitute therefor the sentence: "Allow to cool and make up to 1 liter at 20°C., as described under **1** (**a**)."

(3) **3**, PREPARATION OF FILTER.

Line 3.—Eliminate the sentence: "Dry on a water bath and preserve in a tightly stoppered bottle."

Line 5.—After the term "S. & S." insert the words "or No. 1 F Swedish", making the sentence read: "Stir and pour immediately into a single, 15 cm. No. 590, S. & S. or No. 1 F Swedish folded filter."

At the end of the last paragraph add the sentence: "An ordinary wash bottle serves well for this purpose."

(4) **6**, REAGENTS.

Line 8.—Before "hide powder" insert "air-dry", making the sentence read: "Then for each gram of the air-dry hide powder, so digested, add 1 cc. of 3% chrome alum solution."

(5) **10**, DETERMINATION.

Line 6.—Eliminate the words "precipitates are approximately equivalent in amount" and substitute therefor the words, "if the volume of the precipitate approximately equals or exceeds that of the comparison solution", making the sentence read: "Sulphite-cellulose is held to be present, in the predetermined absence of the synthetic tanning material, Neradol-D, if the volume of the precipitate approximately equals or exceeds that of the comparison solution."

(6) **11**, PREPARATION OF SOLUTION.

Line 4.—Eliminate the word "rapidly" and insert after "20°C." the words "as directed under **1** (a)", making the sentence read: "it may be diluted with water at 80°C., and then cooled to 20°C., as directed under **1** (a)".

(7) **15** (c), *Kaolin.*

Line 1.—Eliminate the semicolon and substitute therefor a comma. Eliminate the words "and dry as under **3**" and substitute therefor the words, "until it complies with the tests given under **3**, dry, and preserve in a tightly stoppered bottle." The corrected paragraph reads: "(c) *Kaolin.*—Digest with dilute hydrochloric acid, wash until it complies with the tests given under **3**, dry, and preserve in a tightly stoppered bottle."

(8) **20**, EXTRACTION.

Lines 15–18.—Eliminate the following: "200 cc. Continue the extraction with water at steam heat, allowing the percolate to run back into the boiling flask. Repeat with 2 successive portions (150–250 cc. each) of water for a total of 14 hours, heating" and substitute therefor "250 cc. and extract for 5 hours. Remove the extract, add 200 cc. of water to the boiling flask and continue the extraction for 9 hours. Throughout the extraction, heat".

Last line of paragraph.—After the word "cool" insert "as directed under **1** (a)". This makes the corrected paragraph read:

"Open the stop-cock (E) and close the side tube (D), add water to the flask (G), if necessary, until it contains about 250 cc., and extract for 5 hours. Remove the extract, add 200 cc. of water to the boiling flask and continue the extraction for 9 hours. Throughout the extraction, heat at such a rate that approximately 330 cc. of water will be condensed per hour. Combine all the extracts in the graduated liter flask in which the first percolate was received. Heat to 80°C., cool as directed under **1** (a) and make up to the mark."

Methods on tanning materials, as changed, adopted as a whole.

VI. LEATHERS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and published in the *Association of Official Agricultural Chemists, Methods*, 1916, 59–61, be changed as follows, and as changed be adopted as the tentative methods of the association for the analysis of leathers:

CHANGES.

(1) **5**, FATS.

Last line of paragraph.—Eliminate the expression "or **7**".

(2) **7**, *Method II.*

Line 1.—Eliminate the sentence "Digest overnight 30 grams of the fat-free leather, obtained under **5**, in approximately 200 cc. of water.", and substitute therefor the sentence: "Extract 30 grams of the leather, prepared as directed under **1**, with petroleum ether as directed under **5**; evaporate the ether from the leather and digest overnight with about 200 cc. of water."

(3) **8**, PREPARATION OF SOLUTION.

Line 2.—Change "normal" to "neutral", making this portion of the sentence read, "a saturated solution of neutral lead acetate".

Line 10.—Eliminate the words "little phenolphthalein" and substitute therefor the words "a few drops of methyl orange", making the sentence read: "Cool, neutralize with solid sodium carbonate, using a few drops of methyl orange as indicator."

(4) **9**, DETERMINATION.

Line 2.—After the expression "**VIII, 25**" insert the phrase "weighing directly as cuprous oxid (**VIII, 26**)" making the sentence read: "Determine dextrose in 50 cc. of the solution, as prepared under **8**, equivalent to 0.5 gram of leather, according to **VIII, 25**, weighing directly as cuprous oxid (**VIII, 26**) and express the result as glucose."

(5) **16**, COMBINED TANNIN.

Line 1.—After "**4**" insert "fats, under **5**", making the sentence read: "Deduct the sum of the percentages of moisture, under **2**, insoluble ash, under **4**, fats, under **5**, soluble solids, under **11**, and hide substance under **15**, from 100."

Methods on leathers, as changed, adopted as a whole.

VII. INSECTICIDES AND FUNGICIDES.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 63–77, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of insecticides and fungicides:

CHANGES.

(1) **3** (a), *Starch indicator.*

At the end of the sentence add the words, "stirring constantly, and discontinue heating immediately after the paste is added", making the sentence read: "pour into about 100 cc. of boiling water, stirring constantly, and discontinue the heating immediately after the paste is added."

(2) **3** (c), *Standard iodin solution.*

Line 5.—Eliminate "400 cc." and substitute therefor the words, "the same volume as that of the aliquot used for the titration in the actual determination", making the sentence read: "Pipette 50 cc. of the arsenious oxid into an Erlenmeyer flask, dilute to about the same volume as that of the aliquot used for the titration in the actual determination, neutralize with sodium bicarbonate, add 4–5 grams in excess, etc."

Line 11.—After the words "*arsenic* oxid (As_2O_5)" insert the sentence: "For the conversion of arsenious oxid (As_2O_3) to arsenic oxid (As_2O_5) multiply by the factor 1.1617."

Line 11.—Eliminate the words "freshly prepared" and substitute therefor the words "the standard". This makes the last three sentences of the paragraph read: "Calculate the value of the standard iodin solution in terms of *arsenious* oxid (As_2O_3) and *arsenic* oxid (As_2O_5). For the conversion of arsenious oxid (As_2O_3) to arsenic oxid (As_2O_5) multiply by the factor 1.1617. Occasionally restandardize the iodin against the standard arsenious oxid solution."

(3) **4**, APPARATUS.

Eliminate this entire paragraph and substitute therefor the following:

"The apparatus used is shown in Fig. 5. The distillation flask rests on a metal gauze which fits over a circular hole in a sheet of heavy asbestos board which, in turn, extends out far enough to protect the sides of the flask from the direct flame of the burner. The first flask which receives the distillate is of 500 cc. capacity and contains 40 cc. of water, the second is of 1000 cc. capacity and contains 100 cc. of water. The volume of water in the first flask should not exceed 40 cc.; otherwise a compound of arsenic will separate when the hot acid vapors strike the cold water which cannot readily be gotten into solution without danger of loss of arsenious chlorid. Both of these flasks should be placed in a pan and kept surrounded with cracked ice and water. The third flask, containing sufficient water to seal the end of the glass tube leading into it, is added as a precaution. It is almost never found to contain any arsenic."

(4) **5**, DETERMINATION.

At the end of the second paragraph after "well cooled" add the sentence: "If the neutral point is passed, add hydrochloric acid until again slightly acid."

(5) FIG. 5. APPARATUS FOR DISTILLATION OF ARSENIC CHLORID.

Change this title to read, "Apparatus for Distillation of Arsenious Chlorid".

(6) TOTAL ARSENIOUS OXID.

Eliminate the first sentence in the parenthesis reading: "The following methods determine arsenic, and antimony if present, as the -ous oxids, As_2O_3 and Sb_2O_3, respectively." and substitute therefor the following: "The following methods determine the arsenic present only in the form of the -ous acid, As_2O_3. They also determine any antimony which may be present in the form of Sb_2O_3." The parenthetical expression will then read: "(The following methods determine the arsenic present only in the form of the -ous acid, As_2O_3. They also determine any antimony which may be present in the form of Sb_2O_3. Ferrous and cuprous salts vitiate the results.)".

(7) **7**, DETERMINATION.

Line 4.—After the word "bath" insert "only as long as is necessary", making the sentence read: "and heat on the steam bath only as long as is necessary to complete solution,".

(8) **29**, DETERMINATION.

Line 4.—After the word "fumes" insert the sentence: "Cool, add a little water and again evaporate till the appearance of white fumes in order to remove the last trace of nitric acid."

(9) **31**, DETERMINATION.

Eliminate the two paragraphs under this heading because of the cross references and substitute the following:

"To 2 grams of the original sample, if in the form of a powder, or 4 grams, if a paste, in a liter Florence flask, add 1 liter of recently boiled water which has been cooled to exactly 32°C. Stopper the flask and place in a water bath kept at 32°C. by means of a thermostat. Digest for 24 hours, shaking hourly for 8 hours during this period. Filter through a dry filter, transfer 250–500 cc. of the *clear* filtrate to an Erlenmeyer flask, add 3 cc. of concentrated sulphuric acid and evaporate on a hot plate. When the volume reaches about 100 cc., add 1 gram of potassium iodid, and continue the boiling until the volume is about 40 cc. Cool, dilute to about 200 cc., remove the excess iodin with N/20 sodium thiosulphate, avoiding the use of starch solution at this point, and proceed as directed under **3** (**c**) beginning with 'neutralize with sodium bicarbonate'. Make correction for the amount of iodin solution necessary to produce the same color, using the same reagent and volume. Calculate and report as per cent of water-soluble arsenic oxid (As_2O_5)."

(10) **59**, CARBONATE AND HYDROXID.—OFFICIAL.

Line 1.—Change the word "the" before the word "weighing" to "a", making the sentence read: "Weigh about 10 grams of the sample from a weighing bottle".

(11) **60**, REAGENTS.

Second line above this heading.—Change "nicotin" to "nicotine".

Disapproved.

(12) **61**, DETERMINATION.

Line 2.—Eliminate the words "if necessary" and substitute therefor the words, "so as to allow it to be powdered", making the sentence read: "or 20 grams of finely powdered tobacco, which has been previously dried at 60°C., so as to allow it to be powdered, into a small beaker."

Line 11.—Change "nicotin" to "nicotine".

Disapproved.

(13) **62** (**a**), *Silicotungstic acid solution.*

At the end of the paragraph add: "(There are several silicotungstic acids. The acids $4H_2O.SiO_2.10WO_3.3H_2O$ and $4H_2O.SiO_2.12WO_3.20H_2O$ do not give crystalline precipitates with nicotin and should not be used.)."

(14) **63**, DETERMINATION.

Lines 2 (two places), 15, 17, 18, 19, 21 and last line of the paragraph.—Change "nicotin" to "nicotine".

Disapproved.

(15) **65**, DETERMINATION.

Line 6.—Insert after the word "titrate" the words "the excess of N/1 sodium hydroxid".

Line 8.—Before the word "Calculate" insert "From the amount of N/1 sodium hydroxid consumed and the weight of the sample".

Line 8.—Change "Calculate" to "calculate".

This makes the last portion of the paragraph read: "and titrate the excess of N/1 sodium hydroxid with N/1 acid, using the litmus solution as indicator. It is necessary to cool the flask before titration with the acid to get a sharp end point with the litmus. From the amount of N/1 sodium hydroxid consumed and the weight of the sample, calculate the per cent of formaldehyde."

(16) **66** (**d**), *50% nitric acid.*

Eliminate "50%" and substitute therefor the word "Dilute", and at the end of the line add the words "(1 to 1)", making the paragraph read, "(**d**) *Dilute nitric acid (1 to 1).*"

(17) **69**, DETERMINATION.

Line 8.—After the word "constantly" insert the sentence: "This should be added at such a rate that about 4 minutes are required in running in the amount necessary, which is about 11 cc. for 1 gram of barium sulphate."

Line 12.—After the words "barium sulphate" insert "using the factor 0.1373", making the sentence read: "Calculate the sulphur from the weight of barium sulphate, using the factor 0.1373."

(18) **72**, THIOSULPHATE SULPHUR.—OFFICIAL.

At the end of the paragraph add: "The value of the iodin solution being given in the terms of arsenious oxid (As_2O_3), multiply the arsenious oxid (As_2O_3) equivalent by the factor 1.296 to obtain the equivalent of thiosulphate sulphur."

Methods on insecticides and fungicides, as changed, adopted as a whole.

VIII. FOODS AND FEEDING STUFFS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and published in the *Association of Official Agricultural Chemists, Methods*, 1916, 79–119, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of foods and feeding stuffs:

CHANGES.

(1) **18**, DETERMINATION OF SUCROSE FROM REDUCING SUGARS BEFORE AND AFTER INVERSION.—TENTATIVE.

Line 9.—Change "245" to "240".

(2) **24** (**b**), REAGENTS.

Change "solution" to "solutions" and "is" to "are", making the sentence read: "(**b**) The solutions used are described under **19**."

(3) **27**, TABLE 1.—MUNSON AND WALKER'S TABLE.

Transfer this table to Chapter "**XXX**, Reference Tables, and designate as "**1**".

(4) **18**, *line 3.*
26, *second paragraph, line 5.*
42, *line 1.*
46, *line 1.*
52, *line 1.*
Eliminate "**27**" and substitute therefor "**XXX, 1**".

(5) **56**, REDUCING SUGARS OTHER THAN DEXTROSE.

Add the word "Tentative" at the end of the line, making the line read, "Reducing Sugars Other Than Dextrose.—Tentative."

Line 4.—Change the number "1.046" to "1.044", making the line read: "Invert sugar, 1.044;".

(6) **57**, PREPARATION OF SOLUTION.

Second line above this heading.—After "Total Sugars.", add "Tentative", making the line read, "Total Sugars.—Tentative."

(7) **58**, DETERMINATION OF REDUCING SUGARS.

Line 1.—Change the words "**26** or **29–34** respectively" to "**25**", making the sentence read: "Proceed as directed under **25**, employing the Soxhlet modification of Fehling's solution and using 25 cc. of the solution".

(8) **59**, SUCROSE.

Line 2.—Change the word "acetic" to "hydrochloric", making the phrase read, "neutralize with hydrochloric acid".

(9) **61**, REAGENT.

Line above this heading.—Change the title to read, "Diastase Method with Subsequent Acid Hydrolysis.—Official."

(10) **64**, DETERMINATION.

Last paragraph, line 2.—Eliminate "**65**" and substitute therefor "**XXX, 2.**"

(11) **65**, TABLE 8.—KRÖBER'S TABLE.

Transfer this table to Chapter **XXX**, Reference Tables, and designate as "**2**".

(12) **67** (**a**), *1.25% sulphuric acid solution.*

Line 1.—Eliminate "1.25%" and substitute therefor "Dilute". Also eliminate the words "Exact strength" and substitute therefor the words, "Contains exactly 1.25 grams of sulphuric acid (H_2SO_4) in 100 cc. as", making the paragraph read: "(**a**) *Dilute sulphuric acid solution.*—Contains exactly 1.25 grams of sulphuric acid (H_2SO_4) in 100 cc. as determined by titration."

(13) **67** (**b**), *1.25% sodium hydroxid solution.*

Line 1.—Eliminate "1.25%" and subsitute therefor the word "Dilute".

Line 1.—Eliminate the words "Exact strength, determined by titration." and substitute therefor the sentences: "Contains exactly 1.25 grams of sodium hydroxid (NaOH) in 100 cc. as determined by titration. This solution should be free or practically free from sodium carbonate." The paragraph will then read: "(**b**) *Dilute sodium*

hydroxid solution.—Contains exactly 1.25 grams of sodium hydroxid (NaOH) in 100 cc. as determined by titration. This solution should be free or practically free from sodium carbonate."

(14) **68**, DETERMINATION.

Line 3.—Before the word "boiling" insert the word "the".

Line 3.—Eliminate "1.25%" and substitute therefor the word "dilute".

Line 4.—After the word "acid" insert "solution, **67** (a)", making the sentence read: "To this residue in a 500 cc. flask add 200 cc. of the boiling dilute sulphuric acid solution, **67** (a)."

Line 10.—Before the word "boiling" insert the word "the".

Line 10.—Eliminate the words "1.25% solution of".

Line 11.—Eliminate the words "free or nearly free from sodium carbonate".

Line 11.—After the word "hydroxid" insert "solution, **67** (b)", making the sentence read: "rinse the substance back into the flask with 200 cc. of the boiling sodium hydroxid solution, **67** (b), boil at once".

Methods on foods and feeding stuffs, as changed, adopted as a whole.

IX. SACCHARINE PRODUCTS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and published in the *Association of Official Agricultural Chemists, Methods*, 1916, 121–39, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of saccharine products:

CHANGES.

(1) **3**, **Drying upon Pumice Stone.—Tentative.**

Line 2.—After the second word "sieve" insert "but not a 1 mm. sieve", making the sentence read: "Prepare pumice stone of two grades of fineness, one of which will pass through a 1 mm. sieve, the other through a 6 mm. sieve, but not a 1 mm. sieve."

(2) **5**, **By Means of a Spindle.—Official.**

Line 13.

7 (a), *By specific gravity at* $\frac{20°\ C.}{4°}$.

Line 3.

Eliminate "**9**" and substitute therefor "**XXX**, **3**".

(3) **7** (b), *By specific gravity at* $\frac{17.5°C.}{17.5°}$.

Eliminate the last two lines, which read: "The pycnometer determination should not be made at any other temperature than $\frac{17.5°C.}{17.5°}$ or $\frac{20°\ C.}{4°}$."

(4) **9**, TABLE 11.—*Densities of solutions of cane sugar at 20°C.*

Eliminate the parenthetical statement in two places. "(This table is the basis for standardizing hydrometers indicating the per cent of sugar at 20°C.)".

Transfer this table to Chapter **XXX**, Reference Tables, and designate as "**3**", and add as "**4**" the correction table given on page 25, Bureau of Standards Circular 19 (1916), entitled "Temperature Corrections to Readings of Saccharometers (standard at 20°C.)".

(5) **10**, *REFRACTOMETER METHOD.—TENTATIVE.*

Line 2.—Eliminate "**11**" and substitute therefor "**XXX, 5**".

Line 3.—Eliminate "**12**" and substitute therefor "**XXX, 6**".

(6) **11**, TABLE 12.—GEERLIG'S TABLE.

Transfer to Chapter **XXX**, Reference Tables, and designate as "**5**".

(7) **12**, TABLE 13.—*Corrections for temperature.*

Transfer to Chapter **XXX**, Reference Tables, and designate as "**6**".

(8) **31**, ALCOHOL IN SIRUPS USED IN CONFECTIONERY ("BRANDY DROPS").—TENTATIVE

Line 9.—Eliminate "**XVI, 5**", and substitute therefor "**XXX, 7**".

(9) **35**, MOISTURE.

Insert the word "Official" at the end of the line, making the heading read, "Moisture.—Official."

(10) After **58** insert a paragraph, **59**, as follows:

59 COMMERCIAL GLUCOSE.—TENTATIVE.

Proceed as directed under **25**.

NOTE: This will necessitate renumbering the remaining headings of the chapter.

(11) BIBLIOGRAPHY.

Reference 9.—Change "p. 60" to "p. 59."

Reference 15.—Change "p. 17" to "p. 21."

Methods on saccharine products, as changed, adopted as a whole.

X. FOOD PRESERVATIVES.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and published in the *Association of Official Agricultural Chemists, Methods*, 1916, 141–54, be changed as follows, and as changed be adopted as the tentative methods of the association for the determination of preservatives in foods:

CHANGES.

(1) **1** (**a**), *Non-alcoholic liquids.*

Line 2.—After the word "substances" insert the words "which cause troublesome emulsions during extractions", making the sentence read: "If gums or mucilaginous substances which cause troublesome emulsions during extraction are present, pipette 100 cc. into a 250 cc. volumetric flask, etc."

(2) **4**, EXTRACTION.

Line 9.—Eliminate the word "an" before the word "emulsion" and substitute therefor the words "a small amount of".

Line 10.—After the word "layer" insert the phrase "where it is frequently broken during the next extraction", making the sentence read: "If a small amount of emulsion still persists, allow it to remain with the aqueous layer, where it is frequently broken during the next extraction."

(3) **13**, *Quantitative Method.*

Line 15.—Eliminate the words "over an alcohol or other sulphur-free flame" and substitute therefor the sentences: "The fusion must be conducted so that gases containing sulphur do not come into contact with the melt. This can be accomplished by using an alcohol flame (Barthel burner) or, if illuminating gas is used, by fitting the crucible into a piece of heavy asbestos board, so that the upper third of the crucible projects above the board, the lower portion of the crucible being in contact with the flame."

(4) **16**, PREPARATION OF SAMPLE.

The second paragraph reading: "In the case of meats * * * * and filter from any insoluble matter" is applicable only to the qualitative tests for formaldehyde. Therefore transfer this paragraph as the first paragraph under **17**.

(5) **20**, *Phenylhydrazin Hydrochlorid and Sodium Nitro-prussid Test.*

Line above this heading.—Change "Rimini Method" to "Rimini's Methods."

Insert "I" before "Phenylhydrazin Hydrochlorid and Sodium Nitro-prussid Test."

(6) **21**, *Phenylhydrazin Hydrochlorid and Potassium Ferricyanid Test.*

Insert "II" before "Phenylhydrazin Hydrochlorid and Potassium Ferricyanid Test."

(7) **22**, *Phenylhydrazin Hydrochlorid and Ferric Chlorid Test.*

Insert "III" before "Phenylhydrazin Hydrochlorid and Ferric Chlorid Test."

Methods on food preservatives, as changed, adopted as a whole.

XI. COLORING MATTERS IN FOODS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 155–69, be changed as follows, and as changed be adopted as the tentative methods of the association for the determination of coloring matters in foods:

CHANGES.

(1) **6**, ORANGE I AND ERYTHROSINE.

Line 1.—After the word "extract" insert "from which some of the colors have been removed," making the sentence read: "Measure, if necessary, the amyl alcohol extract from which some of the colors have been removed, under **5**, then".

(2) **7**, INDIGO CARMINE, AMARANTH AND TARTRAZINE.

Lines 16, 19, 22.—Change the word "hyposulphite" to "hydrosulphite".

(3) **15**, SPECIAL TESTS FOR COAL TAR DYES PERMITTED UNDER THE FEDERAL FOOD AND DRUGS ACT

Lines 5, 13, 15, 16, and paragraph 5, line 2.—Change the word "hyposulphite" to "hydrosulphite".

(4) **20** (C), *Sodium hyposulphite solution.*

Lines 1 and 2.—Change the word "hyposulphite" to "hydrosulphite", making the paragraph read: "(C) *Sodium hydrosulphite solution.*—A freshly prepared 5% solution of 'Blankite', sodium hydrosulphite ($Na_2S_2O_4$)."

(5) **21**, *Sodium hyposulphite.*

Line 7.—Change the word "hyposulphite" to "hydrosulphite" (two places), making the line read: "*Sodium hydrosulphite.*—Add the sodium hydrosulphite solution drop by drop."

(6) **23**, CHLOROPHYLL.

Last line of paragraph.—Eliminate the words "returning to green in a few minutes" and substitute therefor "quickly returning to green", making the sentence read: "The color becomes brown, quickly returning to green."

(7) **26**, COCHINEAL.

Line 13.—Eliminate the words "so sensitive to small amounts" and substitute therefor the words "so characteristic", making the sentence read: "This, however, is not so characteristic as the first test and many fruit colors give tests hardly to be distinguished."

Methods on coloring matters in foods, as changed, adopted as a whole.

XII. METALS IN FOODS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 171–6, be changed as follows, and as changed be adopted as the tentative methods of the association for the determination of metals in foods:

CHANGES.

(1) **1 (b)**, *Sulphuric acid (1 to 2).*

Line 1.—After the word "acid" insert "arsenic-free", making the line read, "(b) *Sulphuric acid, arsenic-free, (1 to 2).*"

(2) **4**, DETERMINATION.

At the end of the paragraph add the following: "Conduct a blank test on the reagents alone and correct the result for any arsenic so found. The blank should not exceed 0.001 mg."

(3) **5**, *Gravimetric Method.—Tentative.*

At the end of the last paragraph add the words "using the factor 0.7881", making the last sentence read: "Weigh as stannic oxid and calculate to metallic tin, using the factor 0.7881."

(4) **9**, ZINC.—TENTATIVE.

At the end of the paragraph add the words "using the factor 0.8034", making the last sentence read: "Calculate the weight of metallic zinc, using the factor 0.8034."

Methods on metals in foods, as changed, adopted as a whole.

XIII. FRUITS AND FRUIT PRODUCTS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis in the *Association of Official Agricultural Chemists, Methods*, 1916, 177–84, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of fruits and fruit products:

CHANGES.

(1) **8**, SULPHATE AND CHLORID.—TENTATIVE.

Change the title to read: "Sulphates and Chlorids.—Tentative."

At the end of the first paragraph add "using the factor 0.7465", making the last sentence of the first paragraph read: "From the weight of barium sulphate calculate the sulphate present as per cent of potassium sulphate, using the factor 0.7465."

(2) **9**, TOTAL ACIDITY.—TENTATIVE.

Line 7.—After the word "in" insert "per cent or", making the phrase read, "expressing the results in per cent or grams per 100 cc."

(3) **19**, *Qualitative Test.—Tentative.*

Eliminate the first three sentences and substitute therefor the following: "Dilute a portion of the sample with water, heat nearly to boiling, add several cc. of dilute sulphuric acid, and then add potassium permanganate solution until all color is destroyed. Cool and test with iodin solution."

(4) **25**, *Method I.—Tentative.*

Insert reference mark after "Method I", and place in bibliography the reference "U. S. Bur. Chem. Circ. 76."

Line 2.—Eliminate "and a dichromate cell".

Lines 22 and 23.—Eliminate "and with a dichromate cell".

(5) **28**, PREPARATION OF SOLUTION.

Line 7.—Eliminate the words "in 100 cc."

(6) **31**, DETERMINATION.

Line 12.—Change "250" to "400".

Line 16.—Change the sentence beginning "After removing from the bath" to read: "After removing from the bath, add rapidly from a burette 25 cc. of the 5% potassium permanganate solution, drop by drop with frequent interruptions, and with constant, vigorous shaking, avoiding a temperature during oxidation exceeding 55°C."

Methods on fruits and fruit products, as changed, adopted as a whole.

XIV. CANNED VEGETABLES.

That the revised methods reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 185–6, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of canned vegetables:

CHANGE.

7, TOTAL ACIDS.—TENTATIVE.

Line 1.—Eliminate the sentence: "Express the result as citric acid; 1 cc. of N/10 alkali is equivalent to 0.0070 gram of crystallized citric acid" and substitute therefor the sentence: "Express the results as number of cc. of N/10 alkali required to neutralize 100 grams of sample."

Methods on canned vegetables, as changed, adopted as a whole.

XV. CEREAL PRODUCTS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists. Methods*, 1916, 187–91, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of cereal products:

CHANGES.

(1) **2, ASH.—OFFICIAL.**

Line 1.—After the word "using" insert "3–", making the phrase read, "using 3–5 grams of the flour."

(2) **8,** *Method I.* (*By nitrogen determination*)*—Tentative.*

Line 5.—Eliminate the words "allow to settle", making the sentence read: "Shake thoroughly once more and filter through a dry, folded filter, returning the first runnings to the filter until a clear filtrate is obtained."

(3) **11, PROTEIN SOLUBLE IN 5 PER CENT POTASSIUM SULPHATE SOLUTION.—TENTATIVE.**

Line 3.—Eliminate the words "let stand overnight".

Line 3.—Change the expression "3 hours" to "1 hour", making the corrected sentence read: "Shake at 30 minute intervals for 3 hours or, better still, agitate at moderate speed in a shaker for 1 hour, let settle 30 minutes, filter, etc."

(4) **14, COLD WATER-SOLUBLE EXTRACT.—TENTATIVE.**

Line 2.—After "10°C." insert the words "or lower", making the phrase read, "200 cc. of water at 10°C. or lower".

Last line of paragraph.—Transpose the words "in an oven at 100°C. for periods of 30 minutes" and place after the word "dry", making the sentence read, "and dry, in an oven at 100°C. for periods of 30 minutes, to constant weight."

(5) **18,** *Quantitative Method.* (*Added Chlorin in Chlorin-Bleached Flours*)*—Tentative.*

Line 6.—After the word "sodium" before the word "hydroxid" insert the words "or of potassium", making the sentence read: "25 grams of sodium or of potassium hydroxid and 15 grams of sodium nitrate per liter."

At the end of this paragraph add the following as a new paragraph: "Special precautions should be taken that the air of the laboratory during the entire operation is not contaminated by chlorin or hydrochloric acid fumes and that all reagents employed are as free as possible from chlorin. In all cases a blank determination should be conducted at the same time and correction introduced if necessary."

Methods on cereal products, as changed, adopted as a whole.

XVI. WINES.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and published in the *Association of Official Agricultural Chemists, Methods*, 1916, 193–242, inclusive, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of wines:

CHANGES.

(1) **XVI. WINES.**

Immediately under the title insert the following parenthetical expression, "(Unless otherwise noted, express results as grams per 100 cc.)".

(2) **3, SPECIFIC GRAVITY.—TENTATIVE.**

Line 1.—At the end of the sentence add: "Standardize the pycnometer as follows: Carefully clean the pycnometer by filling with a saturated solution of chromic acid in concentrated sulphuric acid and allowing to stand for several hours. Empty the pycnometer and rinse thoroughly with water. Then fill it with recently boiled water, previously cooled to 16–18°C., place in a bath of water cooled to the same temperature and allow to warm slowly to 20°C. When the temperature has reached exactly 20°C., strike off the level of the water at the proper point on the pycnometer with a piece of filter paper, adjust the cap in place, remove from the bath, wipe dry with a cloth and, after allowing to stand for 15–20 minutes, weigh. Empty the pycnometer, rinse several times with alcohol and then with ether, allow it to become perfectly dry and weigh. Ascertain the weight of contained water at 20°C. by subtracting the weight of the empty pycnometer from its weight when full, and calculate the weight of contained water at 4°C. by multiplying the results by 1.0018 (determined from the respective densities of water at the two temperatures $\frac{1.00000}{0.99823}$).

"To determine the specific gravity of the wine at $\frac{20°\text{ C.}}{4°}$, cool the latter to 16–18°C., fill the pycnometer, immerse in a water bath cooled to 16–18°C., allow to warm slowly to 20°C., strike off at the mark, adjust the cap, wipe dry and weigh exactly as described above for standardization with water. Subtract the weight of the empty pycnometer from its weight when filled with the wine, and divide the difference by the weight of contained water at 4°C. determined above, the quotient being the specific gravity of the wine at $\frac{20°\text{ C.}}{4°}$."

Mr. H. B. McDonnell (Agricultural Experiment Station, College Park, Md.) made the following recommendation, which was accepted by the Committee on Editing Methods of Analysis and adopted by the association:

3, SPECIFIC GRAVITY.—TENTATIVE.

That the cap of the pycnometer have a capillary opening at the top, or near the top, to provide for the expansion of the liquid.

(3) **4 (a)**, *By volume.*

Line 10.—Eliminate "**5**" and substitute therefor "**XXX, 7**".

(4) **4** (**b**), *Grams per 100 cc.*

Line 2.—Eliminate "**5**" and substitute therefor "**XXX, 7**".

(5) **4** (**d**), *By immersion refractometer.*

Line 3.—Eliminate "**6**" and substitute therefor "**XXX, 8**".

(6) **5**, TABLE 16.—ALCOHOL TABLE.

Transfer this table to Chapter **XXX**, Reference Tables, and designate as "**7**, Alcohol Table."

(7) **6**, TABLE 17.—ALCOHOL TABLE.

Transfer this table to Chapter **XXX**, Reference Tables, and designate as "**8**, Alcohol Table."

Mr. S. H. Ross (Bureau of Chemistry, Washington, D. C.) made the following recommendation, which was seconded by Mr. E. G. Grab (Bureau of Chemistry, Washington, D. C.), and adopted by the association:

8, *Method II. (By Oxidation with Dichromate)—Tentative.*

Line 5.—After the word "stirring" insert "except that before the addition of the silver carbonate the residue is transferred with hot water to a 100 cc. graduated flask". The last portion of the paragraph will then read as follows: "Proceed from this point as directed under **XIX, 6**, beginning with the clause 'evaporate almost to dryness, with frequent stirring', except that before the addition of the silver carbonate the residue is transferred with hot water to a 100 cc. graduated flask. Observe the precautions given concerning the temperature at which all evaporations are to be made."

(8) **11**, **From the Specific Gravity of the Dealcoholized Wine.—Tentative.**

Line 7.—Eliminate "**IX, 9**" and substitute therefor "**XXX, 3**".

(9) **14** (**b**), *Sweet wines.*

Line 4.—Change "245" to "240".

(10) **23**, SULPHURIC ACID.—TENTATIVE.

Last line of paragraph.—After "(SO_3)" insert "using the factor 0.3430".

Methods on wines, as changed, adopted as a whole.

XVII. DISTILLED LIQUORS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and published in the *Association of Official Agricultural Chemists, Methods*, 1916, 243–8, inclusive, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of distilled liquors:

CHANGES.

(1) **1**, SPECIFIC GRAVITY.—TENTATIVE.

Line 1.—After the word "pycnometer" insert "as directed under **XVI, 3**".

Line 1.—After the word "or" insert "by means of", making the paragraph read: "Determine the specific gravity at $\frac{20^\circ C.}{4^\circ}$ by means of a pycnometer as directed under **XVI, 3**, or by means of a small, accurately graduated hydrometer."

(2) **2**, ALCOHOL BY WEIGHT.—OFFICIAL.

Line 4.—Eliminate "**XVI, 5**" and substitute therefor "**XXX, 7**".

Line 8.—Eliminate "**XVI, 6**" and substitute therefor "**XXX, 8**".

(3) **3**, *Method I.—Official.*

Line 2.—Eliminate "**XVI, 5**" and substitute therefor "**XXX, 7**".

(4) **4**, *Method II.—Tentative.*

Line 3.—Eliminate "**XVI, 5**" and substitute therefor "**XXX, 7**".

Line 7.—Eliminate "**XVI, 6**" and substitute therefor "**XXX, 8**".

(5) **11** (a), *Standard furfural solution.*

Line 1.—Omit "(a)", so that the heading will read: "Standard furfural solution."

At the end of the paragraph add the sentence: "The strong furfural solution will retain its strength but the dilute solutions will not."

(6) **11** (b), *Furfural-free alcohol.*

Eliminate the entire line.

(7) **13** (a), *Purified carbon tetrachlorid.*

Add as a second paragraph: "The refuse carbon tetrachlorid after titration is purified for further work by collecting in a large bottle, adding concentrated sodium hydroxid solution, shaking, washing with tap water until the washings are neutral to phenolphthalein, and distilling."

Methods on distilled liquors, as changed, adopted as a whole.

XVIII. BEERS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and published in the *Association of Official Agricultural Chemists, Methods*, 1916, 249–51, inclusive, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of beers:

CHANGES.

(1) **XVIII. BEERS.**

Immediately under the heading "**XVIII. BEERS.**" insert in small print, "(Unless otherwise noted, express results as grams per 100 cc.)".

(2) **3**, SPECIFIC GRAVITY.—TENTATIVE.

Line 1.—After the word "pycnometer" insert "as directed under **XVI, 3**", making the sentence read: "Determine the specific gravity at $\frac{20^\circ C.}{4^\circ}$ by means of a pycnometer, as directed under **XVI, 3.**"

(3) **7**, *Method III.—Tentative.*

Line 7.—Eliminate "**IX, 9**" and substitute therefor "**XXX, 3**".

(4) **18**, PROTEIN.—OFFICIAL.

Line 3.—Before the word "multiply" insert the word "and".

Line 3.—Eliminate the words "and calculate the percentage of protein" and substitute therefor the words "to obtain the equivalent of protein". This makes the corrected phrase read, "and multiply the result by 6.25 to obtain the equivalent of protein."

Methods on beers, as changed, adopted as a whole.

XIX. VINEGARS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and published in the *Association of Official Agricultural Chemists, Methods*, 1916, 253–8, inclusive, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of vinegars:

CHANGES.

(1) **3**, SPECIFIC GRAVITY.—TENTATIVE.

Line 1.—After the word "pycnometer" insert "as directed under **XVI, 3**", making the sentence read: "Determine the specific gravity at $\frac{20^\circ C.}{4^\circ}$ by means of a pycnometer, as directed under **XVI, 3**."

(2) **4**, ALCOHOL.—TENTATIVE.

Line 5.—Eliminate "**XVI, 5**" and substitute therefor "**XXX, 7**".

(3) **11**, LEAD PRECIPITATE.—TENTATIVE.

Line 1.—After the expression "20%" insert "neutral", making the line read, "To 10 cc. of the sample in a test tube, add 2 cc. of 20% neutral lead acetate solution".

Methods on vinegars, as changed, adopted as a whole.

XX. FLAVORING EXTRACTS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 259–69, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of flavoring extracts:

CHANGES.

(1) **1**, SPECIFIC GRAVITY.—TENTATIVE.

Line 1.—At the end of the sentence add the words "as directed under **XVI, 3**".

(2) **4**, PREPARATION OF SOLUTION.

Line 4.—After the expression "8%" insert the word "neutral".

Line 7.—Eliminate the word "normal".

(3) **6**, NORMAL LEAD NUMBER.—TENTATIVE.

Change the title to read: "Lead Number.—Tentative."

Lines 6 and 9.—Eliminate the word "normal".

(4) **7**, TOTAL SOLIDS.—TENTATIVE.

8, ASH.—OFFICIAL.

Change the word "grams" to "cc."

(5) **17**, SPECIFIC GRAVITY.—TENTATIVE.

Line 1.—At the end of the sentence add the words "as directed under **XVI, 3**".

(6) **18**, ALCOHOL.—TENTATIVE.

Line 10.—Change the reference "**XVI, 5**" to "**XXX, 7**".

(7) **22** (a), *Aldehyde-free alcohol.*

Line 2.—Insert after the word "for" the words "at least".

(8) **23**, DETERMINATION.

Line 8.—After the expression "2 cc." insert "(or a suitable amount)".

(9) **32**, SPECIFIC GRAVITY.—TENTATIVE.

Line 1.—At the end of the sentence insert the words "as directed under **XVI, 3**."

Methods on flavoring extracts, as changed, adopted as a whole.

XXI. MEAT AND MEAT PRODUCTS.

That the methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 271–86, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of meat and meat products:

CHANGES.

(1) **25**, APPARATUS.

Line 8.—After the word "tubing" add the words "to prevent fracture, but arrange the latter so that it will not interfere with the free exit of gas."

(2) **26**, DETERMINATION.

Line 16.—Insert the phrase, "Note the volume of nitric oxid contained in the tube, the temperature, and barometric pressure, and".

Line 16.—Change "Calculate" to "calculate", making the sentence read: "Note the volume of nitric oxid contained in the tube, the temperature, and barometric pressure, and calculate the volume of nitric oxid at 0°C. and 760 mm. pressure."

Dr. P. F. Trowbridge (Agricultural Experiment Station, Agricultural College, N. Dak.) and Dr. F. C. Cook (Bureau of Chemistry, Washington, D. C.) made the following recommendations, which were adopted by the association:

(1) **1**, PREPARATION OF SAMPLE.—TENTATIVE.
2, MOISTURE.—TENTATIVE.
3, ASH.—OFFICIAL.
4, CRUDE FAT OR ETHER EXTRACT.—OFFICIAL.
5, TOTAL PHOSPHORUS.—TENTATIVE.

Retain these paragraphs with the old headings and numbers.

(2) **8**, TOTAL NITROGEN.—OFFICIAL.
Change "8" to "6".

(3) **14**, APPARATUS.
Change "**14**" to "**7**".

(4) **15**, DETERMINATION.
Change "**15**" to "**8**".

(5) **24**, REAGENT.
Change "**24**" to "**9**".

(6) **25**, APPARATUS.
Change "**25**" to "**10**".

(7) **26**, DETERMINATION.
Change "**26**" to "**11**".

(8) **27**, REAGENTS.
Change "**27**" to "**12**".

(9) **28**, DETERMINATION.
Change "**28**" to "**13**".

(10) **17**, *Qualitative Test.—Tentative.*
Change "**17**" to "**14**".

(11) **18**, *Mayrhofer Method, Price Modification.—Tentative.*
Change "**18**" to "**15**".

(12) **19**, *Qualitative Test.—Tentative.*
Change "**19**" to "**16**".

(13) **20**, PREPARATION OF SOLUTION.
Change "**20**" to "**17**".

(14) **21**, DETERMINATION.
Change "**21**" to "**18**".

(15) **22**, REAGENTS.
Change "**22**" to "**19**".

(16) **23**, DETERMINATION.
Change "**23**" to "**20**".

(17) **29**, PRESERVATIVES.—TENTATIVE.
Change "**29**" to "**21**".

(18) **30**, METALS.—TENTATIVE.

Change "**30**" to "**22**".

(19) **31**, COLORING MATTERS.—TENTATIVE.

Change "**31**" to "**23**".

(20) **9**, SOLUBLE AND INSOLUBLE NITROGEN.—TENTATIVE.

Change "**9**" to "**24**".

Eliminate the heading "Soluble and Insoluble Nitrogen.—Tentative" and substitute therefor the general heading "Water Extract.—Tentative." and the subheading "Preparation of Solution." Include in this paragraph all of the material given in **9** (old number) through the word "thoroughly", fifth line from the end of the paragraph. The amended paragraph will then read as follows:

24 WATER EXTRACT.—TENTATIVE.

PREPARATION OF SOLUTION.

Exhaust 7–25 grams of the sample depending upon the water content in the following manner: Weigh into a 150 cc. beaker, add 5–10 cc. of cold (15°C.) ammonia-free water and stir to a homogeneous paste. Then add 50 cc. of cold water, stir every 3 minutes for 15 minutes, let stand for 2–3 minutes and decant the liquid upon a quantitative filter, collecting the filtrate in a 500 cc. graduated flask. Drain the beaker, pressing out the liquid from the meat residue by the aid of a glass rod. Add to the residue in the beaker 50 cc. of cold water, stir for 5 minutes, allow to stand 2–3 minutes, and decant as before. If a considerable portion of the meat is carried over onto the filter, transfer it back to the beaker by means of a glass rod. Repeat the extractions, using the following additional amounts of cold water: 50, 50, 25, 25, 25, and 25 cc. After the last extraction transfer the entire insoluble portion to the filter and wash with three 10 cc. portions of water, allowing the material to drain thoroughly after each addition of water. Dilute to the mark and mix thoroughly.

(21) **10**, CONNECTIVE TISSUE NITROGEN.—TENTATIVE.

Eliminate this paragraph and substitute therefor the following paragraph, numbering it "**25**":

25 SOLUBLE AND INSOLUBLE NITROGEN.

Determine the total nitrogen in a 50 cc. aliquot of the solution obtained under **24**, proceeding as directed under **I**, **18**, **21** or **23**. Subtract the percentage of soluble nitrogen from the percentage of total nitrogen, **6**, to obtain the percentage of insoluble nitrogen. To obtain the percentage of insoluble protein, multiply the percentage of insoluble nitrogen by 6.25.

(22) **11**, COAGULABLE PROTEINS.—TENTATIVE.

Change "**11**" to "**26**", and change the heading "Coagulable Proteins.—Tentative." to "Coagulable Nitrogen.—Tentative."

(23) **12**, *Modified Tannin-Salt Method.—Tentative.*

Line above this heading.—Change to "Proteose, Peptone and Gelatin Nitrogen.", and change "**12**" to "**27**".

(24) **13**, MEAT BASES.—TENTATIVE.

Change "**13**" to "**28**".

(25) **16**, CREATIN.—OFFICIAL.

Change "**16**" to "**29**".

(26) **44**, REAGENTS.
Change "**44**" to "**30**".

(27) **45**, APPARATUS.
Change "**45**" to "**31**".

(28) **46**, DETERMINATION.
Change "**46**" to "**32**".

(29) Add three new paragraphs, **33**, **34** and **35**, to read as follows:

33 *Sörenson Formol Titration Method.—Tentative.*

To 20 cc. of the filtrate from **26**, or 20 cc. of a solution containing an extract of the meat (in some cases a larger volume may be necessary), add 10 cc. of a freshly prepared phenolphthalein-formol mixture (50 cc. of commercial formol containing 1 cc. of a 0.5% solution of phenolphthalein in 50% alcohol, exactly neutralized with N/5 barium or sodium hydroxid). Titrate the mixture with N/5 barium hydroxid solution until a distinct red color appears, add a slight known excess of N/5 barium hydroxid and titrate back to neutrality with N/5 hydrochloric acid. Conduct a blank titration with the same reagents, using 20 cc. of water in place of the solution to be tested. From the amount of N/5 barium hydroxid required to neutralize the mixture, corrected for the amount used in the blank titration, calculate the amount of amino nitrogen present (including ammonia if this has not been removed). One cc. of N/5 barium hydroxid is equivalent to 2.8 mg. of amino nitrogen.

34 TOTAL SOLUBLE PHOSPHORUS.—TENTATIVE.

Evaporate to dryness 50 cc. of the water extract prepared under **24**, moisten the residue with 10 cc. of concentrated sulphuric acid, add a few drops of nitric acid and heat on a hot plate until all of the organic matter is destroyed. Add 100 cc. of water, boil for a few minutes and proceed as directed under **I**, **6**.

35 SEPARATION OF SOLUBLE INORGANIC AND ORGANIC PHOSPHORUS.—TENTATIVE.

To 500 cc. of the extract, prepared as directed under **24**, add 50 cc. of magnesia mixture [**I**, **4** (**c**)] and proceed as directed under **37**.

(30) **6**, PREPARATION OF SOLUTIONS.
Line above this heading.—Eliminate this line and substitute therefor "Soluble Phosphorus in Blood, Brain and Glandular Organs.—Tentative."
Change "**6**" to "**36**".

(31) **7**, DETERMINATION.
Change "**7**" to "**37**".

(32) **32**, PREPARATION OF SAMPLE.—TENTATIVE.
Change "**32**" to "**38**".

(33) MOISTURE.—TENTATIVE.
Change "**33**" to "**39**".

(34) **34**, ASH.—OFFICIAL.
Change "**34**" to "**40**".

(35) **35**, TOTAL PHOSPHORUS.—TENTATIVE.
Change "**35**" to "**41**".

(36) **36**, CHLORIN.—TENTATIVE.
Change "**36**" to "**42**".

(37) **37**, FAT.—TENTATIVE.
Change "**37**" to "**43**".

(38) **38**, TOTAL NITROGEN.—OFFICIAL.
Change "**38**" to "**44**".

(39) **41**, AMMONIA.—TENTATIVE.
Change "**41**" to "**45**".
Change this paragraph to read as follows:
"Introduce 1 gram of pasty extracts or 2–3 grams of fluid extracts into tube (B) of the Folin apparatus and proceed as directed under **8**."

(40) **39**, INSOLUBLE PROTEIN.—TENTATIVE.
Change this heading to read, "Insoluble Nitrogen.—Tentative.", and change "**39**" to "**46**".

(41) **40**, COAGULABLE PROTEIN.—TENTATIVE.
Change this heading to read, "Coagulable Nitrogen.—Tentative.", and change "**40**" to "**47**".

(42) **42**, PROTEOSES AND GELATIN.—TENTATIVE.
Change "**42**" to "**48**".

(43) **43**, GELATIN.—TENTATIVE.
Change "**43**" to "**49**".

(44) Add a new paragraph, **50**, to read as follows:

50 AMINO NITROGEN.—TENTATIVE.

Proceed as directed under **32** or **33**, using an aliquot of the filtrate from **47**.

(45) **47**, ACID ALCOHOL-SOLUBLE NITROGEN.—TENTATIVE.
Change "**47**" to "**51**".

(46) **48**, CREATIN.—OFFICIAL.
Change "**48**" to "**52**".

(47) **49**, CREATININ.—OFFICIAL.
Change "**49**" to "**53**".

(48) **50**, *Cook Method.—Tentative.*
Change "**50**" to "**55**".

(49) **51**, SUGAR.—TENTATIVE.
Change "**51**" to "**56**".

(50) **52**, PRESERVATIVES.—TENTATIVE.
Change "**52**" to "**57**".

(51) **53**, METALS.—TENTATIVE.
Change "**53**" to "**58**".

Methods on meat and meat products, as changed, adopted as a whole.

XXII. DAIRY PRODUCTS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 287–98, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of dairy products:

CHANGES.

(1) **8**, REAGENTS.

Line above this heading.—Change "Tentative" to "Official".

(2) **12**, *Roese-Gottlieb Method.—Official.*

Line 13.—After the word "parts" insert the words "free from suspended water".

(3) **16 (b)**, *Ash.*

Line 8.—Eliminate the last sentence of paragraph and substitute therefor the following: "The acetic serum ash multiplied by the factor 1.021 equals the sour serum ash (dilution of the acetic serum being 2%)."

(4) **17 (a)**, *Zeiss immersion refractometer reading.*

Line 1.—Insert bibliography reference "5" after "Zeiss immersion refractometer reading."

(5) **17 (b)**, *Ash.*

Line 1.—Change "Ash[5]" to "Ash[6]".

(6) BIBLIOGRAPHY.

After line 5 add the following as a new reference: "[5]Z. offent. Chem., 1903, **9**: 173."

Line 6.—Change bibliography reference "5" to "6".

Methods on dairy products, as changed, adopted as a whole.

XXIII. FATS AND OILS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 299–315, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of edible fats and oils:

CHANGES.

(1) Change the type in the title for **2**, line above **3**, titles for **5**, **6** and **7**, to conform with **11**½(italics).

(2) **2**, At $\frac{20°C.}{4°}$.—Tentative.

Line 1.—After the word "pycnometer" add the words "as directed under **XVI, 3**."

(3) **4**, DETERMINATION.

Line 1.—Eliminate the expression "dried at the temperature of boiling water" and insert the word "dry" before the word "flask", making the phrase read: "Fill the dry flask with the dry, hot, freshly filtered fat".

(4) **5**, General Directions.—Tentative.

Last paragraph, line 1.—Eliminate the word "directly" and after the word "gravity" add "and in the same direction."

(5) **15 (b)**, *N/10 sodium thiosulphate.*

Line 1.—After the heading "N/10 sodium thiosulphate.—" insert the sentence: "Dissolve 24.82 grams of recrystallized sodium thiosulphate ($Na_2SO_3.5H_2O$) in water and dilute to 1 liter." The paragraph will then read: "(**b**) *N/10 sodium thiosulphate.*—Dissolve 24.82 grams of recrystallized sodium thiosulphate ($Na_2SO_3.5H_2O$) in water and dilute to 1 liter. Standardize this solution, etc."

(6) **15 (e)**, *N/10 potassium dichromate.*

Line 1.—After the heading "N/10 potassium dichromate.—" insert the sentence: "Dissolve 4.903 grams of potassium dichromate in water and dilute to 1 liter." The paragraph will then read: "(**e**) *N/10 potassium dichromate.*—Dissolve 4.903 grams of potassium dichromate in water and dilute to 1 liter. The dichromate solution should be checked against pure iron."

(7) **1**, REAGENTS.

Change paragraph number "**1**" to "**19**".

(8) **24**, SAPONIFICATION.

At the end of the last paragraph add the sentence: "Remove the last traces of alcohol by waving the flask briskly, mouth down, or better, by a current of air free from carbon dioxid."

(9) **28**, *Polenske Method.—Tentative.*

Second paragraph, line 5.—Eliminate the words "as obtained above" and substitute therefor the words "obtained as above upon a 5 gram sample".

Methods on fats and oils, as changed, adopted as a whole.

XXIV. SPICES AND OTHER CONDIMENTS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 317–26, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of spices and other condiments:

CHANGES.

(1) **24**, SOLIDS.—TENTATIVE.

Line 3.—Eliminate the words "at 100°C."

(2) **35**, TOTAL SOLIDS.—TENTATIVE.

Line 1.—Eliminate the word "platinum".

(3) **49**, APPARATUS.

Line above this heading.—Eliminate the last three words and substitute therefor "Sauce and Paste".

Eliminate (**a**), (**b**) and (**c**) and substitute therefor the following:

"(**a**) *Compound microscope.*—Equipped with apochromatic objectives and compensating oculars, giving magnifications of approximately 90, 180, and 500 diameters. These magnifications can be obtained by the use of 16 and 8 mm. Zeiss apochromatic objectives with X6 and X18 Zeiss compensating oculars, or their equivalents, such as the Spencer 16 and 8 mm. apochromatic objectives with Spencer X10 and X20 compensating oculars, the draw-tube of the microscope being adjusted as directed below.

"(**b**) *Thoma-Zeiss blood counting cell.*

"(**c**) *Howard mold counting cell.*—Constructed like a blood counting cell but with the inner disk (which need not be ruled) about 19 mm. in diameter."

(4) **50**, MOLDS.—TENTATIVE.

Line 1.—Eliminate the expression "Thoma-Zeiss" and substitute the word "Howard".

Third paragraph, line 1.—Insert after the word "with" the words "a magnification of", making the sentence read: "Place the slide under the microscope and examine with a magnification of about 90 diameters, etc."

At the end of the paragraph add the following: "This area is of vital importance and may be obtained by adjusting the draw-tube to the proper length as determined by actual measurement of the field, a 16 mm. Zeiss apochromatic objective with a Zeiss X6 compensating ocular, or a Spencer 16 mm. apochromatic objective with a Spencer X10 compensating ocular, or their equivalents, being used to obtain the proper magnification."

(5) **51**, YEASTS AND SPORES.—TENTATIVE.

Second paragraph, line 7.—Eliminate the last sentence of the paragraph and substitute therefor the following: "Make the count with a magnification of about 180, to obtain which the following combinations, or their equivalents, should be employed: 8 mm. Zeiss apochromatic objective with X6 Zeiss compensating ocular, or an 8 mm. Spencer apochromatic objective with X10 Spencer compensating ocular with draw-tube not extended.

(6) **52**, BACTERIA.—TENTATIVE.

Line 2.—Eliminate the sentence beginning "Use a magnification of about 500", and substitute therefor the following: "Employ a magnification of about 500, which may be obtained by the use of an 8 mm. Zeiss apochromatic objective with an X18 Zeiss compensating ocular with draw-tube not extended, or an 8 mm. Spencer apochromatic objective with an X20 Spencer compensating ocular with a tube-length of 190, or their equivalents."

Line 4.—Eliminate the sentence beginning "Because of the somewhat" and ending "being about 375."

Mr. B. J. Howard (Bureau of Chemistry, Washington, D. C.) made the following recommendation:

49, 50, 51, 52, MICRO-ANALYSIS OF TOMATO PULP, KETCHUP, PUREE AND SAUCE (PASTE).

That the methods for the analysis of these products, **49**, **50**, **51** and **52**, be transferred to the chapter on canned vegetables.

Adopted.

Methods on spices and other condiments, as changed, adopted as a whole.

XXV. CACAO PRODUCTS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 327–30, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of cacao products:

CHANGE.

15, SUCROSE AND LACTOSE.—TENTATIVE.

Line 9.—Before the word "liquid" insert the word "added".

Methods on cacao products, as changed, adopted as a whole.

XXVI. COFFEES.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 331–4, be adopted as the official and tentative methods of the association for the analysis of coffees.

Adopted.

XXVII. TEA.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 335–7, be adopted as the official and tentative methods of the association for the analysis of tea.

Adopted.

XXVIII. BAKING POWDERS AND THEIR INGREDIENTS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and published in the *Association of Official Agricultural Chemists, Methods*, 1916, 339–50, be changed as follows, and as changed be adopted as the official and tentative methods of the association for the analysis of baking powders and baking chemicals:

CHANGES.

(1) **XXVIII. BAKING POWDERS AND THEIR INGREDIENTS.**

Change the title of the chapter to "Baking Powders and Baking Chemicals."

(2) **3** (**a**), *50% potassium hydroxid solution.*

Eliminate the entire paragraph and substitute therefor the following: "(**a**) *Potassium hydroxid solution.*—Dissolve 25 grams of potassium hydroxid in 50 cc. of water."

(3) **4, 5, 7, 8.**

Make uniform use of parentheses with letters for designating parts of apparatus in the text.

Methods on baking powders and their ingredients, as changed, adopted as a whole.

XXIX. DRUGS.

That the revised methods, as reported by the Committee on Editing Methods of Analysis and printed in the *Association of Official Agricultural Chemists, Methods*, 1916, 351–66, be changed as follows, and as changed be adopted as the tentative methods of the association for the analysis of drugs:

CHANGES.

(1) **1**, PREPARATION OF SAMPLE AND SOLUTION.—TENTATIVE.

(**b**) *Line 8.*—At the end of the sentence ending with the word "extraction" insert the following sentence: "Any caffein acetanilid mixture observable about the apex of the delivery tube of the separatory, edge of filter and tip of funnel should be very carefully recovered by judicious washing with chloroform, such washings being subsequently united with the main portion."

(**c**) *Line 8.*—After the word "in" insert the words "the aqueous".

(2) **2** (**a**), *Standard bromid-bromate solution.*

Line 4.—Insert after the word "recrystallized" the words "and dried".

(3) **3**, CAFFEIN.—TENTATIVE.

First paragraph, last line.—After the word "stand" insert the words "in the open".

Second paragraph, line 11.—After the word "liquid" insert the words "deep claret".

(4) **9**, ANTIPYRIN.—TENTATIVE.

Line 14.—After the word "above" insert the sentence: "Recover any crystalline product separating about the tip of the delivery tube and funnel and edge of filter by judicious washing with chloroform."

Insert in fine print between the first and second paragraphs the following:

"The use of alcohol-free chloroform in connection with the halogenation of antipyrin is necessary in order to preclude the formation of iodoform, the presence of which in the composite residue "a" would vitiate the result."

(5) **10**, CAFFEIN.—TENTATIVE.

Line 1 of (2).—Eliminate the word "Hydrolysis" and substitute therefor the words "Hydrolytic treatment".

(6) **12**, DETERMINATION.

Line 6.—After the word "thoroughly" insert the words "by rotating the liquid".

Line 7.—Eliminate the word "shaking" and substitute therefor the words "rotating the liquid".

Line 14.—After the word "thoroughly" insert the words "by rotating the mixture".

Line 3 of (2).—After the word "transfer" eliminate the words "together with the filter" and substitute therefor the words "the precipitate together with the filter, likewise any particles of the precipitate remaining in the graduated flask".

(7) **29**, QUININ SULPHATE.—TENTATIVE.

At the end of the paragraph add a separate paragraph in fine print as follows:

"If the morphin sulphate present is contaminated with codein sulphate, the latter will be separated and weighed with the quinin."

(8) **30**, MORPHIN SULPHATE.—TENTATIVE.

After the second paragraph add two additional paragraphs in fine print as follows:

"Despite all precautions looking to the exclusion of impurities from the morphin as weighed, the amount of this substance thus determined will usually be greater than that found volumetrically. In order to insure the greatest possible accuracy in volumetric operations on alkaloidal residues like quinin, morphin and codein, it is suggested that, whenever possible, the strength of the standard acid used be checked by titration against the pure alkaloid under examination.

"In the various operations involving fixation and subsequent liberation of morphin by means of fixed alkali and ammonium chlorid, the most careful attention should be paid to the manner of adding the reagents, since any undue excess of either might nullify the entire procedure. Any large excess of sodium hydroxid would naturally require for its reduction a correspondingly large amount of ammonium chlorid, the latter in turn yielding its equivalent of hydroxid, relatively large quantities of which through interaction with sodium chlorid tend to inhibit any permanent liberation of alkaloid and thus prevent complete extraction. Furthermore, ammonium chlorid in large amount operates retentively on the morphin in solution, due in part possibly to the formation of an alkaloidal hydrochlorid."

(9) **39**, PREPARATION OF SOLUTIONS.

(b) *Line 2.*—After the word "sample" add "(a)".

(c) *Line 2.*—After the word "sample" add "(a)".

(d) *Line 2.*—After the word "sample" add "(a)".

(10) **40**, DETERMINATION.

Second paragraph, line 2.—After the word "sample" insert "**39 (b)**".

Second paragraph, line 3.—After the word "sample" insert "**39 (c)**".

Second paragraph, line 5.—After the expression "U. S. P. pepsin per cc." insert "**39 (d)**".

Second paragraph, line 8.—After the expression "pepsin per cc." insert "**38 (b)**".

(11) **44**, DISTILLATION.—TENTATIVE.

Line 3.—After "200°C." insert "in such a way that the mercury bulb shall be opposite the side tube of the flask and the 175° mark below the cork."

Methods on drugs, as changed, adopted as a whole.

Respectfully submitted,

R. E. DOOLITTLE,
JOHN PHILLIPS STREET,
W. A. WITHERS,
A. F. SEEKER,
G. W. HOOVER,
Committee on Editing Methods of Analysis.

The report was adopted with a rising vote of thanks to the Committee on Editing Methods of Analysis and to the chairman of the committee for their splendid work and for the fine report they presented.

As chairman of the Committee on Editing Methods of Analysis, Mr. Doolittle took occasion to thank not only the members of the association but outside chemists as well for the valuable service they rendered the committee.

A motion was made, seconded and adopted that the Committee on Editing Methods of Analysis be continued and that it be instructed to incorporate in the methods the changes adopted at this meeting.

Mr. Doolittle called attention to the fact that quite a number of tentative methods appear in the revised methods, which the Committee on Editing Methods of Analysis feel have been before the association long enough either to be made official or rejected. The committee, however, did not know how to handle the matter and so Mr. Doolittle, as chairman of the committee, asked the association for instructions.

A motion was adopted that this matter be left to the discretion of the Committee on Editing Methods of Analysis.

Dr. P. F. Trowbridge (Agricultural Experiment Station, Agricultural College, N. Dak.) raised the question of the advisability of designating methods by the names of authors. Considerable discussion ensued and, while the association approved the general principle of eliminating such names wherever possible, the following motion introduced by Dr. Trowbridge was adopted:

That the Committee on Editing Methods of Analysis be given authority to include or omit the names of authors in connection with the titles of methods, as in their judgment seems best.

The meeting adjourned at 12.30 P. M. to reconvene at 1.30 P. M.

WEDNESDAY—AFTERNOON SESSION.

REPORT OF SECRETARY-TREASURER FOR

By C. L. Alsberg (Bureau of Chemistry,

GENERAL

RECEIPTS.

1915		
Nov. 17	Bank balance	$181.04
1916		
April 15	Refund on letterheads ordered from Charles G. Stott and Company	.75
Nov. 16	1914–15 dues from 2 States (Alabama and Kansas)	4.00
	Dues for the year 1915–16 from 84 Federal, State, and municipal organizations	168.00
	1916–17 dues from Porto Rico	2.00
		$355.79

JOURNAL

RECEIPTS.

1915		
Dec. 8	Subscription from Kansas State Board of Health	$4.00
1916		
Feb. 18	Subscription from Pittsburgh Bureau of Food Inspection (F. C. Buckmaster)	4.00
April 17	Subscription from Laboratory Inland Revenue, Vancouver, B. C. (J. A. Dawson)	4.00
April 17	Subscription from Tennessee State Department of Agriculture (J. W. Sample)	4.00
	Deficit, paid from Secretary-Treasurer account	14.82
		$30.82

THE YEAR ENDING NOVEMBER 22, 1916.

Washington, D. C.), *Secretary-Treasurer.*

ACCOUNT.

DISBURSEMENTS.

1915			
Nov. 17	Telephone calls, Raleigh Hotel, 1915 meeting		$1.10
Nov. 17	Tips, Raleigh Hotel		2.50
1916			
Jan. 10	Post office box rent (check No. 37)		1.00
Feb. 3	Printing circulars and bills (check No. 39)		17.75
Feb. 7	Postage (check No. 41)		5.00
Feb. 11	Postage (check No. 43)		3.00
April 4	Post office box rent (check No. 45)		1.00
April 4	Postage (check No. 46)		2.00
April 14	Letterheads (check No. 48)		7.50
April 18	1000 special request envelopes (check No. 49)		22.00
April 24	Postage (check No. 50)		2.00
July 7	Post office box rent (check No. 51)		1.00
Aug. 24	500 envelopes (check No. 55)		.75
Sept. 25	Post office box rent (check No. 57)		1.00
Oct. 16	Postage (check No. 58)		4.25
Oct. 30	One ream typewriter paper (check No. 59)		1.80
Nov. 15	Printing 800 announcements, 1916 meeting (check No. 60)		23.25
Nov. 16	350 badges (check No. 61)		23.00
	Journal account		14.82
Nov. 14	Bank balance	$275.30	
	Less checks out	54.23	
			221.07
			$355.79

ACCOUNT.

DISBURSEMENTS.

1915		
Dec. 4	Williams & Wilkins Co. (Subscription Kansas State Board of Health, check No. 36)	$4.00
1916		
Feb. 2	Williams & Wilkins Co. (Subscription F. C. Buckmaster, check No. 38)	4.00
Feb. 8	Williams & Wilkins Co. (Subscription J. A. Dawson, check No. 42)	4.00
Feb. 26	Williams & Wilkins Co. (Subscription J. W. Sample, check No. 44)	4.00
April 6	Expressage on methods manuscript (check No. 47)	.30
Aug. 19	Postage (check No. 52)	5.00
Aug. 23	Telegram (check No. 53)	.41
Aug. 24	Telegram (check No. 54)	.77
Sept. 14	Clerical work (Miss Ferriter, check No. 56)	8.34
		$30.82

The undersigned committee has examined the above report and finds it correct.

JOHN PHILLIPS STREET,
CHAS. B. LIPMAN,
B. B. ROSS,
Auditing Committee.

Approved.

REPORT ON THE JOURNAL.

By C. L. ALSBERG (Bureau of Chemistry, Washington, D. C.), *Chairman, Board of Editors.*

It is possible to report only on Volume I, the last number of which was issued in June. There were over nine hundred subscriptions to that volume, and a deficit of only two hundred and seventy-five dollars, as shown in the statement received from the publishers. The statement from the publishers was not quite clear in certain respects, so an expert accountant is at present auditing the books. When Volume II began, we had a loss of one hundred and fifty to two hundred subscribers from failure to renew. Since that time, there has been a steady increase in the number of subscriptions. We receive from ten to twenty-five new subscriptions a month without special effort or solicitation. The present subscription list is approximately eight hundred. The publishers anticipate that by spring or summer the list of subscribers will reach one thousand or twelve hundred. The indications are that probably there will be no deficit for Volume II, so I think we can feel that the success of *The Journal* is now assured. I think that a deficit of two hundred and seventy-five dollars on the first volume of a scientific journal of this nature is a good showing for the present year.

There have been a good many subscriptions received from all over the world, some from South America, South Africa, Australia, and from each of the British Colonies. A number of subscriptions have also been received from France, England and Russia, and I dare say that this number will be increased considerably at the end of the war.

In reference to the methods, you will be interested to learn that the publisher is ready to reprint the methods as a separate volume. At present it is impossible to fix a definite price for the book, since we do not know how much it is going to cost to make these revisions and to incorporate into the revised methods the action taken at this meeting. Of course, I suppose it would be desirable to include everything done at this meeting. It is really very difficult to say definitely what it is going to cost, but we hope to be able to secure a very reasonable rate for the members of the association.

The editors of *The Journal* have been endeavoring to dispose of the hitherto unpublished proceedings of the association and the revision of the methods. Judging from present prospects, we hope to have all the proceedings up to date by midwinter or early spring, including the proceedings of this meeting. If it were not for the portion of the 1915 proceedings still unpublished, we should be able to print the proceedings of this meeting much more rapidly than will be the case. At any rate, by midwinter or spring of the coming year we hope to be thoroughly

up to date, when *The Journal* will be in a position to accept scientific communications of a research nature, apart from the proceedings. The editors of *The Journal* hope that, when *The Journal* begins to accept such communications, it may devote its pages to publishing research papers of a high grade, apart from reports of referees.

It is the intention of the editors of *The Journal*, unless otherwise instructed by this association, to give preference to papers dealing with methods of analysis. It is not their intention, however, unless you wish otherwise, to reject good work in general agricultural chemistry when such work is presented for publication in *The Journal*. It is merely our intention to give preference, so far as space may require a discrimination, to analytical papers rather than to papers of a general chemical nature.

Few editorial changes have been made in the reports of referees, except where there were obvious errors, misstatements or unnecessary paragraphs, because the Board of Editors was uncertain as to the extent of its authority in such matters. The editors of *The Journal* have accordingly asked the Executive Committee for instructions, and in compliance with this request the committee has drawn up the following resolution:

Resolved, That the Board of Editors of the *Journal of the Association of Official Agricultural Chemists* be authorized to edit the reports of referees, and if any material changes are deemed advisable, that such proposed changes be submitted to the Chairman of the Committee on Recommendations of Referees and Revision of Methods, and be referred to the proper Subcommittee A, B, or C for approval. The manuscript, as edited, shall be submitted to the referee for approval before publication. The Board of Editors is authorized to prepare a type form for the reports of referees which shall be followed by the referee wherever practicable, so that uniformity in the work of referees may be promoted and the work of editing such reports may be facilitated.

The Board of Editors would welcome criticisms, advice, and recommendations, formal or informal, from the floor now or in writing at any time.

The report, together with the resolution contained therein, was unanimously adopted by the association.

Dr. C. L. Alsberg, on behalf of the Executive Committee, recommended that the distribution of referees be revised. The essential features of the revision involved the grouping of the subjects more logically, the dropping of the general subject of food adulteration, and the appointment of a referee on micro-analytical methods. The recommendations of the committee were adopted.

Dr. P. F. Trowbridge made the following recommendations:

(1) That the referee on meat and meat products make a special study of starch, glycogen, and the two nitrate methods.

Adopted.

(2) That an associate referee on meat extracts be appointed and that he be instructed to study during the next year the glycerol method, the sugar method, and the acid alcohol-soluble nitrogen method.

Adopted.

REPORT OF COMMITTEE TO COOPERATE WITH OTHER COMMITTEES ON FOOD DEFINITIONS AND STANDARDS[1].

Your committee desires to submit the following report of the activities of the joint committee on food definitions and standards during the past association year.

Three meetings of the joint committee have been held during this year. Of these, the first of the year (the seventh conference of the committee since its organization) was held in Washington, D. C., January 17 to 20, 1916; the second, in Detroit, August 5 to 10, 1916; the third, in Washington, D. C., November 16 to 18, 1916.

These meetings were in part given up to hearings which were either granted upon request or were held upon published announcement at the committee's initiative. Other hearings authorized by the joint committee were held by subcommittees. Among the subjects of these hearings were: The grading of milk and cream, condensed milk products, dried milk, homogenized and emulsified milk products, cheese, evaporated apples, spices, citrus fruits and baking powders. Conferences also upon the subject of grades of canned foods have been held with various manufacturing and distributing organizations.

Various subcommittees have under consideration important groups of food products, some of which have been preliminarily considered by the joint committee, with respect to which the work is not yet sufficiently advanced to warrant announcement at this time.

The following schedules have been adopted during the year by the joint committee for recommendation to the Association of American Dairy, Food and Drug Officials, the Association of Official Agricultural Chemists and the Secretary of Agriculture for their approval, and have been approved by the association first named, at its meeting of August 10, 1916.

PRINCIPLES OF STANDARDIZATION.

The general considerations which have guided the joint committee on definitions and standards in preparing definitions and standards for food products are the following:

[1] Presented by William Frear.

(1) The definitions are framed so as to include those facts of material, quality, origin and mode of preparation that are essential to distinguish the food named. These definitions may or may not be accompanied by specifications of limits of physical quality and chemical composition characteristic of the food defined.

Foods vary in composition with differences in season and soil, and because of variations in manufacturing operations, and they may be associated with small amounts of foreign substances, owing to imperfect conditions of production. The specifcations of limits of physical quality and chemical composition are so drawn as to provide for variations due to such causes and of degree commonly accepted as reasonable.

(2) The definitions are so framed as to exclude from the articles defined substances not included in the definitions.

(3) A term defined in any of the several schedules has the same meaning wherever it is used in any schedule.

(4) The names of food products herein defined preferably agree with existing American usage as known to the consumer.

MILK PRODUCTS.

Definitions adopted by the joint committee on definitions and standards, August 6, 1916:

Sweetened condensed milk is the product resulting from the evaporation of a considerable portion of the water from milk to which sugar (sucrose) has been added. It contains, all tolerances being allowed for, not less than twenty-eight per cent (28%) of total milk solids, and not less than eight per cent (8%) of milk fat.

Condensed skimmed milk, evaporated skimmed milk, concentrated skimmed milk, is the product resulting from the evaporation of a considerable portion of the water from skimmed milk, and contains, all tolerances being allowed for, not less than twenty per cent (20%) of milk solids.

Sweetened condensed skimmed milk, sweetened evaporated skimmed milk, sweetened concentrated skimmed milk, is the product resulting from the evaporation of a considerable portion of the water from skimmed milk to which sugar (sucrose) has been added. It contains, all tolerances being allowed for, not less than twenty-eight per cent (28%) of milk solids.

Dried milk is the product resulting from the removal of water from milk, and contains, all tolerances being allowed for, not less than twenty-six per cent (26%) of milk fat, and not more than five per cent (5%) of moisture.

Dried skimmed milk is the product resulting from the removal of water from skimmed milk and contains, all tolerances being allowed for, not more than five per cent (5%) of moisture.

Malted milk is the product made by combining whole milk with the liquid separated from a mash of ground barley malt and wheat flour, with or without the addition of sodium chlorid, sodium bicarbonate and potassium bicarbonate, in such manner as to secure the full enzymic action of the malt extract, and by removing water. The resulting product contains not less than seven and one-half per cent (7.5%) of butter fat and not more than three and one-half per cent (3.5%) of moisture.

EDIBLE VEGETABLE FATS AND OILS.

Definitions adopted by the joint committee on definitions and standards, November 18, 1916:

Edible fats and edible oils are such glycerides of the fatty acids as are recognized to be wholesome foods. They are dry and sweet in flavor and odor.

Cacao butter, cocoa butter, is the edible fat obtained from sound cacao beans (*Theobroma cacao* L.), either before or after roasting.

Coconut oil, copra oil, is the edible oil obtained from the kernels of the coconut (*Cocos nucifera* L. or *Cocos butyracea* L.).

Cochin oil is coconut oil prepared in Cochin (Malabar).

Ceylon oil is coconut oil prepared in Ceylon.

Corn oil, maize oil, is the edible oil obtained from the germ of Indian corn, maize (*Zea mays* L.).

Cottonseed oil is the edible oil obtained from the seed of the cotton plant (*Gossypium herbaceum*, L.) or from the seed of other species of *Gossypium*.

Olive oil, sweet oil, is the edible oil obtained from the sound, mature fruit of the olive tree (*Olea europaea* L.).

Palm kernel oil is the edible oil obtained from the kernels of the fruit of the palm tree (*Elaeis guineensis* L. or *Elaeis melanococca* Gärt.).

Peanut oil, arachis oil, earthnut oil, is the edible oil obtained from the peanut (*Arachis hypogæa* L.).

Poppy seed oil is the edible oil obtained from the seeds of the poppy (*Papaver somniferum* L.).

Rape seed oil, rape oil, colza oil, is the edible oil obtained from the seed of the rape plant (*Brassica napus* L.), or from the seed of closely related *Brassica* species, which yields oils similar in composition and character to the oil obtained from the seed of *Brassica napus* L.

Soy bean oil, soy oil, soja oil, is the edible oil obtained from the seed of the soy bean plant (*Glycine soja* L., *Soja hispida*, Sieb et Zucc., *Soja max.* (L.) Piper).

Sesame oil, gingili oil, teel oil, benne oil, is the edible oil obtained from the seed of the sesame plant (*Sesamum indicum*, De Candolle, *Sesamum radiatum*, Schum and Thonn, *Sesamum orientale* L.).

Sunflower oil is the edible oil obtained from the seed of the sunflower (*Helianthus annuus* L.).

EVAPORATED APPLES.

Definition adopted by the joint committee on definitions and standards, August 7, 1916:

Evaporated apples are evaporated fruit made from peeled, cored and sliced apples and contain not more than twenty-four per cent (24%) of moisture.

Pending the official adoption by this association of perfected methods for estimating moisture in evaporated apples, the following trade method shall be employed:

Dry a representative unminced sample for 4 hours at the temperature of boiling water and determine the loss in weight.

In addition to the foregoing, partial schedules for "Soda Water Flavors" and for "Soda, Soda Water" were recommended to and approved by the Association of American Dairy, Food and Drug Officials in August, 1916. Owing, however, to the publication of the results of an investigation which may require the modification of a fundamental conclusion involving these schedules, the joint committee has deemed it wise to withhold them from presentation at this time, so that they may be further considered before the approving acts of the several authorities concerned shall have been completed.

The joint committee has prepared for your present action two groups of definitions and standards, in addition to those above given. They deal with macaroni and related products and with baking powders.

MACARONI, SPAGHETTI, VERMICELLI, FLOUR MACARONI, FLOUR SPAGHETTI, FLOUR VERMICELLI.

Definitions and standards adopted by the joint committee on definitions and standards, November 18, 1916:

Macaroni, spaghetti, vermicelli are dried pastes made of the semolina of hard wheat. They contain not more than thirteen and one-half per cent (13.5%) of moisture.

Flour macaroni, flour spaghetti, flour vermicelli are dried pastes made of flour or of a mixture of flour and semolina.

They contain not more than thirteen and one-half per cent (13.5%) of moisture.

BAKING POWDER.

Definition adopted by the joint committee on definitions and standards, November 18, 1916:

Baking powder is the leavening agent produced by the mixing of an acid reacting material[1] and sodium bicarbonate, with or without starch or flour. It yields not less than twelve per cent (12%) of available carbon dioxid.

The acid reacting materials in baking powder are: (1) Tartaric acid or its acid salts; (2) acid salts of phosphoric acid; (3) compounds of aluminium; or (4), any combination in substantial proportions of the foregoing.

COMMENTS.

The milk products schedule is, with the exception of the definition and standard for sweetened condensed milk, entirely new matter. The definition for sweetened condensed milk, though modified in phrasing, is substantially a reaffirmation of that previously proclaimed[2], with a very slight increase of the fat minimum.

The schedule for edible vegetable fats and oils represents a revision of the corresponding schedule of Circular 19. The revision differs from the former schedule in having a group definition comprehending a statement of the chemical character of these products and, in addition, of those qualities that determine edibility; in the omission from the specific definitions of all matters covered by the group definition; in the dropping of separate standards for cold-pressed and virgin oils; in the omission, for the present, of statements of chemical limits, those of

[1] The announcement of the amount of calcium sulphate which reacts as an acid reacting material in baking powder is reserved pending further investigation.
Baking powder materials should be as free from metallic impurities as it is feasible for a manufacturer to make them. The announcement of the limits for arsenic, lead, zinc and fluorids is reserved pending further investigation.

[2] U. S. Dept. Agr., Office of the Secretary, Circ. 19.

Circular 19 having been found confusing because of the general overlapping of the so-called "constants" of different oils, and the wide variation of these characters in individual oils without corresponding, clearly defined alteration of their food values; and, finally, in the addition of a definition for soy bean oil.

The definition and standard for evaporated apples is a revision of the corresponding definition and standard of Circular 19. It differs therefrom in the inclusion of "slicing" as a process in the manufacture, in a reduction of the moisture maximum, and in a fuller description of the commercial method of moisture determination for this product. Permit us, in this connection, to note the need for a special study by this association of the problem of evolving a more exact and yet convenient method for this determination.

The schedule for macaroni and related products proposes what is deemed the best solution of the difficulties arising from the manufacture and sale of alimentary pastes made of wheat flour, or of mixtures thereof with semolina, in the form of macaroni, vermicelli and spaghetti normally made exclusively from the semolina of hard wheat.

The definition and standard for baking powder deals fundamentally with a group of products that have, from time to time, been the subjects of much discussion, and which present many phases of composition. The definition with its accompanying declarations provides for the use, as ingredients of baking powder, of all materials generally employed as such ingredients. It suggests the suitable subordinate classification according to the acid or acid-reacting substance or substances used; and, finally, it leaves the way open to the introduction, under suitable label declarations, of wholesome food materials which may for any reason seem desirable, providing such introduction does not in any way contravene the Federal Food and Drugs Act, and does not reduce the yield of available carbon dioxid below the accompanying specification. This specification is in accordance with the producers' recommendations and not below the limit fixed by those State laws in which a limit for this leavening reaction product has been given.

Respectfully submitted,

WILLIAM FREAR,
JULIUS HORTVET,
JOHN PHILLIPS STREET,
Committee to Cooperate with Other Committees on Food Definitions and Standards.

Approved.

REPORT OF COMMITTEE ON AVAILABILITY OF PHOSPHORIC ACID IN BASIC SLAG[1].

Your committee desires to submit the following report of progress made during the past association year.

The Rhode Island Agricultural Experiment Station has completed the work it has been conducting in cooperation with your committee and has submitted its final report. This includes pot and field experiments with millet and rape. The year 1916 was devoted to observing the after-effects in the field of the phosphoric applications made during 1915.

The Hawaii, Texas, New York (Ithaca), and North Dakota Agricultural Experiment Stations have submitted no further data than that referred to in the last report of your committee[2].

The Massachusetts Agricultural Experiment Station reports that three series of pot experiments with rape and millet have been completed and that one season's growth of rape with the different phosphates has been attained in the field. The results, however, could not be reported prior to this meeting because of contemplated chemical work on the crops.

At the Pennsylvania Agricultural Experiment Station clover and timothy were grown on the field plots in 1916 without any phosphatic application since 1913. It is probable that a new application of phosphatic materials will be made in the near future.

A report from the Illinois Agricultural Experiment Station includes results of pot experiments conducted during 1915 and 1916 with clover, soy beans, wheat, millet and rape. Data obtained with phosphates other than those furnished by the committee are also included.

Owing to inequalities still existing in the fields selected for the experiments at the North Carolina and Virginia Agricultural Experiment Stations, these stations postponed the application of phosphates. Pot experiments have been started at the North Carolina Agricultural Experiment Station with prospect of a final report in 1917.

Your committee feels that the referee on phosphoric acid should be instructed to continue the study of methods for determining the availability of phosphoric acid in slag, and chemical matters pertaining thereto, so that the association may have at hand the data necessary to aid it in the adoption of an availability method as soon as the results of the vegetation experiments are obtained. Sufficient reports are already in the hands of your committee to be of service to the referee on phosphoric acid in his chemical investigations. It seems unnecessary to wait until all of the vegetation results are at hand before tentative methods of analysis are submitted to the association.

---

[1] Presented by P. F. Trowbridge.
[2] *J. Assoc. Official Agr. Chemists*, 1917, 3: 104.

It is therefore recommended by your committee that this association instruct its referee on phosphoric acid to give prominent attention to the question of methods of determining available phosphoric acid in slag, the chemical ingredients influencing the same, and the bibliography on the subject.

C. B. WILLIAMS, H. D. HASKINS,
B. L. HARTWELL, C. G. HOPKINS,
J. A. BIZZELL,
Committee on Availability of Phosphoric Acid in Basic Slag.

Adopted.

REPORT OF COMMITTEE ON AMENDMENTS TO THE CONSTITUTION AND BY-LAWS.

By B. B. Ross (Polytechnic Institute, Auburn, Ala.), *Chairman.*

Your committee recommends the adoption of the Constitution and By-laws in the following amended form:

CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

ARTICLE I.

This association shall be known as the ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS OF NORTH AMERICA. The objects of the association shall be (1) to secure uniformity and accuracy in the methods, results, and modes of statement of analysis of fertilizers, soils, cattle foods, dairy products, human foods, medicinal plants, drugs, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

ARTICLE II.

Analytical chemists connected with the United States Department of Agriculture, or with any State, provincial, or national agricultural experiment station or agricultural college, or with any State, provincial, or national institution or body in North America charged with official control of the materials named in Article I, shall alone be eligible *ex officio* to active membership. Analytical chemists connected with municipal laboratories charged with control of any of the materials or subjects named in Article I shall be eligible *ex officio* to associate membership. Active members of the association who lose their right to such membership by retiring from positions indicated above as requisite for eligibility to active membership may become eligible *ex officio* to associate membership. Persons may be elected to honorary membership by the two-thirds vote of those present at any regular meeting of the association.

ARTICLE III.

The officers of the association shall consist of a President, a Vice-President, and a Secretary, who shall also act as Treasurer, and these officers shall be elected annually from active members. The duties of said officers shall be those that generally pertain to such positions. These officers, together with two other active members, to be elected by the association, shall constitute the Executive Committee. The special duties of the officers of the association shall be further defined, when necessary, by the Executive Committee. There shall be appointed by the President, on the recommendation of the Executive Committee, a committee of nine members, which shall be designated as a Committee on Recommendations of Referees, one-third of the membership of which shall be appointed at intervals of two years to serve six years. The chairman of the committee shall be elected by the members of the committee from among their own number. The chairman shall divide the nine members into subcommittees (A, B, and C) and shall assign to each subcommittee the reports and subjects which it shall consider. At the annual meeting there shall be appointed by the President, upon the recommendation of the Committee on Recommendations of Referees, from among the members[1] of the association, a referee and associate referees for each of the subjects to be considered by the association. It shall be the duty of these referees to prepare and distribute samples and standard reagents to members of the association and others desiring the same, to furnish blanks for tabulating analyses, and to present at the annual meeting the results of the work done, discussion thereof, and recommendations for methods to be based thereon.

ARTICLE IV.

The annual meeting of the association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the Executive Committee, and announcement thereof shall be made at least three months prior to the time of said meeting. Special meetings may be called by the Executive Committee when in its judgment it shall be necessary.

ARTICLE V.

All proposed changes or amendments to this constitution shall be presented in writing and read in full to the association not later than the first day of the regular annual meeting, shall be referred to the

[1] When used without any qualifications, construed by the association to mean either active or associate members.

Executive Committee, and after a report from this committee may be adopted on the succeeding day by a vote of three-fourths of the active members present.

Adopted.

BY-LAWS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

(1) Any amendment to these by-laws or changes therein may be proposed and adopted in the same manner as amendments to the constitution, but only a two-thirds vote of the active members present shall be required for their adoption.

(2) These by-laws or any portion of them may be suspended at any regular meeting of the association without previous notice by a vote of three-fourths of the active members present.

(3) Only such colleges, experiment stations, bureaus, boards, or other institutions whose members are active members of this association shall be entitled to enter motions and vote.

(4) On general questions before the whole association, each college, experiment station, etc., as qualified above, shall be entitled to one vote only. In voting upon questions involving methods of analysis, definitions, nomenclature and laws or regulations relating to materials mentioned in Article I of the Constitution, each of the said institutions shall be entitled to vote only upon questions relating to those materials over which said institution exercises official control.

(5) A method shall not be adopted as official or an official method be amended until such method or amendment has been recommended as official for at least two annual meetings by the appropriate referee.

(6) No changes shall be made in the methods of analysis used in official inspection until an opportunity shall have been given all active members having charge of the particular inspection affected to test the proposed changes.

(7) A method shall not be adopted as tentative or a tentative method amended until such method or amendment has been reported by the appropriate referee and published in the proceedings of the association.

(8) When any officer, referee, or associate referee ceases to be eligible for membership in the association, his office shall be considered vacant and a successor may be appointed by the Executive Committee to continue in office until the next following regular meeting. The Executive Committee shall also have authority to fill vacancies occurring in any other manner.

(9) Chemists and others interested in the objects of the association may attend its meetings, take part in its discussions, and present papers, if permission is secured from the Executive Committee.

(10) Each college, experiment station, bureau, board or other institution entitled to representation in the association shall contribute annually $5.00 prior to the first of January following the regular annual meetings.

Adopted.

A motion was made, seconded and adopted that the Executive Committee give careful consideration to definitions for "official method" and "tentative method", and formulate definitions to be presented next year, and that at the present time the words be without definition.

REPORT OF COMMITTEE ON NOMINATIONS.

By C. C. McDonnell (Bureau of Chemistry, Washington, D. C.), *Chairman.*

The committee submitted the following nominations for officers for the year ending November, 1917: President, J. K. Haywood of Washington, D. C.; vice-president, P. F. Trowbridge of North Dakota; secretary-treasurer, C. L. Alsberg of Washington, D. C.; additional members of the executive committee, B. B. Ross of Alabama, and H. C. Lythgoe of Massachusetts.

The secretary was instructed to cast the unanimous ballot of the association for these officers.

REPORT OF COMMITTEE ON RESOLUTIONS[1].

By William Frear (Agricultural Experiment Station, State College, Pa.), *Chairman.*

We have lost from our number, through death since the last meeting, four members: Robert James Davidson, on December 19, 1915; Eugene Woldemar Hilgard, on January 8, 1916; George Edward Patrick, on March 22, 1916; and Thomas Cuthbert Trescot, on April 14, 1916. We mourn the loss of these tried and true associates, and desire to record in some permanent way our appreciation of them.

Owing to the long interval between the time of Professor Davidson's death and this meeting, the officers of this association thought best to draft and present to his widow the following memorial:

[1] Presented by W. A. Withers.

WHEREAS Providence has removed from membership in this association our honored former president and coworker, Robert James Davidson of Virginia: Therefore be it

Resolved, That in the death of Professor Davidson the Association of Official Agricultural Chemists has lost one of its staunchest and most trusted workers, and its members, an associate admired for his thoroughness and steadfastness of judgment, and beloved for his modesty and rare kindliness of spirit. He shot no barbed shafts of wit; he wielded no double-edged sword of satire; nor opened his lips to utter a word of disparagement of others; but wherever he was, there gathered a group drawn by the lodestone of his character, the smile of friendship upon his often pain-worn face, his sympathetic heart, and his keen discernment and high appreciation of what was good and true in others.

Through a quarter of a century he has been constantly contributing to the work of the association, rendering service of especial merit in relation to the methods of analysis for insecticides and fungicides, and has acted as the referee on these methods and upon those for determining nitrogen, and also, for some years, as chairman of one of the three most responsible committees on recommendations of referees and revision of methods.

In 1903, in recognition of his labors for the association and of his high standing in the chemical profession, he was chosen president of the association. In 1907 he was made the delegate of the association to report to the International Congress of Applied Chemistry at the London meeting, the association's judgment concerning the unification of terms to be used in reporting analytical results. His contributions to the American literature of agricultural chemistry include some of its best work upon the subjects of the chemistry of tobacco, and of fruits and fruit juices.

Resolved, further, That this association express to the Virginia Agricultural and Mechanical College and Agricultural Experiment Station its regret at the loss of so able and useful an officer, teacher, and investigator, and to Mrs. Davidson its sympathy in her sorrow.

January 19, 1916.

Your committee recommends the adoption of the following resolution:

Resolved, That the Association of Official Agricultural Chemists reaffirms the memorial to Robert James Davidson drafted by its officers, and directs that it be spread upon the minutes, and that the secretary send to Mrs. Davidson a copy of this resolution.

Although Professor Hilgard, owing to the burden of administrative duties and his remoteness from our meeting place, and, in later years, because of his failing health and advancing age, was unable to attend many of the sessions, he was nevertheless an *ex officio* member, and maintained to his death a warm interest in such of our work as pertained to his special field of study. Your committee recommends the adoption of the following resolution as a brief memorial of his service:

Resolved, That in the death of Professor Eugene Woldemar Hilgard, Ph. D., LL. D., America has lost her leading pioneer in the domain of soil chemistry. To his long service, comprehensive labors, keen insight, sense of proportion, stability of judgment,

clearness of expression and wealth of inspiration, American agricultural chemists owe a lasting debt. The Association of Official Agricultural Chemists directs that this resolution of appreciation be placed upon its permanent records, and that its secretary transmit a copy thereof through the University of California to Dr. Hilgard's family

The adoption of the following resolution, memorial to Professor Patrick, is recommended:

Resolved, That in the death of Professor George Edward Patrick, from 1873 to 1874, instructor in chemistry in Cornell University; from 1874 to 1883, professor of chemistry in the University of Kansas; from 1888 to 1895, chemist of the Iowa Agricultural Experiment Station; from 1895 to 1901, assistant chemist; and from 1901 to his death, Chief of the Dairy Laboratory of the Bureau of Chemistry; author of the Patrick method for milk fat determination; deviser of the copper distillation flask for the Kjeldahl nitrogen method; sometime referee of this association; skilled craftsman in the application of analytical methods to the examination of dairy products, this association has lost a valued collaborator and a comrade, whose sterling worth we have tested through twenty years of acquaintance.

Resolved, further, That this memorial be spread upon the minutes, and a copy transmitted to his nearest of kin.

Your committee recommends the adoption also of the following resolution, memorial to Mr. Thomas Cuthbert Trescot:

Resolved, That in the death of Thomas Cuthbert Trescot, assistant chemist in the Bureau of Chemistry since 1884, for many years Chief of the Nitrogen Laboratory of the Bureau of Chemistry, sometime referee of this association, expert analyst of nitrogenous compounds, this association has lost a valued collaborator and a highly esteemed friend.

Resolved, further, That this resolution be spread upon the minutes, and a copy thereof transmitted to his widow

Your committee further recommends that the Board of Editors be instructed to have prepared and to print in *The Journal* of this association suitable biographical sketches of these deceased members.

Adopted by rising vote.

ROBERT JAMES DAVIDSON.

Robert James Davidson, Dean of the Department of Applied Science and Professor of Chemistry at the Virginia Polytechnic Institute, died very suddenly at his home in Blacksburg, Virginia, December 19, 1915. He was born in Armagh, Ireland, April 3, 1862, of Scotch-Irish parents. He was only an infant when his father died and the family moved to Manchester, England, where he received his early education.

When he was about sixteen years of age he went to Georgetown, S. C., and made his home with an uncle. In 1882 he matriculated at the South Carolina College at Columbia, where he completed a four year course in

three years, doing extra work on the campus to maintain himself while at college. He received the degree of Bachelor of Science in 1885, and returned the following session as tutor in chemistry and as secretary of the faculty, pursuing at the same time advanced studies in chemistry. He received his Master of Arts degree in 1887. In 1888 he was appointed Assistant Professor of Chemistry and Assistant Chemist of the South Carolina Experiment Station. In 1891 he was elected Professor of Chemistry in the Virginia Agricultural and Mechanical College at Blacksburg, Virginia, and also Chemist of the Virginia Agricultural Experiment Station. He was married on May 2, 1892 to Miss Anna McBryde. His wife and two daughters survive him. In 1904 he was elected to the position of Dean of the Department of Applied Science in the Virginia Polytechnic Institute, where he served with great efficiency until the day of his death.

His duties as an instructor made heavy demands upon his time and energy, yet he kept in touch with the progress of science. He was a Fellow of the American Association for the Advancement of Science; a member of the American Chemical Society; and a member of the Association of Official Agricultural Chemists, attending the meetings of these societies whenever possible. He contributed articles along agricultural chemical lines to the publications of the Virginia Agricultural Experiment Station. He always looked forward with pleasure to the meetings of the Association of Official Agricultural Chemists and attended nearly all of them for a period of over twenty years. He was always active in all the work of the association, serving as referee on several subjects and cooperating in others. In 1903 he served the association as its president.

Professor Davidson was endowed with exceptional ability as a teacher, and his life and character was a source of inspiration and encouragement to all who came into contact with him.

W. B. ELLETT.

EUGENE WOLDEMAR HILGARD.

AN APPRECIATION.

Eugene Woldemar Hilgard was born at Zweibrucken, Rhenish Bavaria, January 5, 1833. His father came to America, with his family, three years later and settled on a farm in Illinois, and, owing to the crude nature of the public schools there, undertook personally the training of his son. Thus Eugene was ready for the university at sixteen, and was sent to Germany. He studied at Heidelberg, receiving there the doctor's degree in 1853, at the age of twenty. That degree was reissued to him

by Heidelberg in 1903 as a "Golden Degree" in recognition of his distinguished services to science in fifty years.

After taking his degree, Dr. Hilgard went to Spain, where he met Miss J. Alexandrino Bello, whom he married in 1860. In 1855 he returned to America, where he did geological work in Mississippi until 1858, when he was appointed State Mineralogist of that State. During the Civil War, Hilgard was a scientific adviser to the Confederacy. In 1866 he was made Professor of Chemistry in the University of Mississippi, and later Professor of Zoology, Geology and Botany. In 1872 he was made Professor of Geology and Natural History in the University of Michigan. That title amused him much then and in after years, as I remember his gleeful chuckle in telling about it. In 1874 he was called to the University of California, where he remained until his death. He founded the first agricultural experiment station, developed instruction in agriculture and was Dean of the College of Agriculture and Director of the Agricultural Experiment Station, and enjoyed a position of trust and honor among his colleagues.

In recognition of his splendid scholarly attainments, the honorary degree of Doctor of Laws was conferred on him by four universities, viz., Mississippi, Columbia, Michigan and California. From 1910 until the time of his death he was Emeritus Professor of Agricultural Chemistry, but in that period never lost his interest and keen enjoyment in scientific work. He died, January 8, 1916, soon after celebrating his eighty-third birthday. He is survived by two daughters, Alice and Marie Louise, Mrs. Hilgard having died several years before her husband. Their only son died at the early age of twenty-one, a tragic event which saddened the latter half of Hilgard's life.

In the history of that dimly defined realm known as Agricultural Science, still a more or less chaotic mass of erudition, and in its formative stages, few names stand out in such bold relief as that of Eugene Woldemar Hilgard. To those whose way of life has been fashioned in the grooves of that field of activity, Hilgard is perhaps as well known and by them as much honored as anyone who had preceded or anyone who has followed him. His name stands there for integrity and high purpose, for its association with the most attractive of the amenities of polite social intercourse, for idealism in scholarship and a fair modicum of realization thereof, for unswerving adherence to the truth as scholars see it, for indomitable courage, persistence, and perseverance, for undaunted determination to try and try again even in the face of failure, to lead oneself as well as others in the right ways as man sees them, for an insight amounting almost to foresight, for a gentleness, and a dignity, and a charm withal that taken in those other lights bespoke rare balance, poise, and an accentuation of the unusual in man. His name, too, stands

to his erstwhile fellow workers for the exploratory temperament in its most praiseworthy expression, for the blazer of trails, for the fearless pioneer and delver into the regions beyond the ken of man. And yet that same name speaks to them of simplicity, of a true humanness, of an ability to lead and instruct which have gained its quondam possessor an unequivocal place in the respect and affection of his fellowmen, and the generations which follow.

Hilgard was a man of about average height, slender, graceful in carriage and courtly in manner. Broadly educated beyond most of his contemporaries in science, his excellent classical education and his masterful knowledge of several languages rendered him a deep thinker and a conversationalist of singular charm and attractiveness. By birth and breeding a gentleman, he won the hearts of his friends and acquaintances by his inimitably delightful manner in social intercourse. But like all forceful men he had his other side. He was possessed of a grim determination, an unyielding tenacity, a bold combativeness which those who engaged in battle with him will never forget. In espousing and championing a cause he gave himself to it in unstinted measure, and fought for the truth as he saw it with an energy, a whole-souled intrepidity and alertness which will always be remembered by his adversaries. It might be said of Hilgard as Ingersoll said of Roger Conkling, "He knew his friends; his enemies knew him." Thus was Hilgard a leader in his generation. Kind, charming, lovable, he was tireless in spite of a lifetime of delicate health, unafraid, unflinching in his advocacy of a principle, a theory, an idea. That his masterful, tenacious, forceful side at times made him overzealous and occasionally blinded him to some side of an issue is only what one would expect of men, however strong, but essentially Hilgard was possessed of a blending of strong characteristics, rare even among leaders, in which we may truly say he had the qualities of his defects. He was a man through and through, and in his long, eventful career we glimpse a vision of a life in his home as well as without it which men may well emulate. A devoted husband and father beyond the ken of ordinary men, Hilgard loved and was beloved and was inspiration.

As a teacher Hilgard was kindly, patient, resourceful, and devoted. He loved the seeker after knowledge and spared no pains to give to the earnest student of his own ample store of erudition in unrestrained measure and in impressive manner. The educators of today may well study Hilgard, the teacher, to learn the value of a broad education to the scholar and the builder of scholars. He enjoyed teaching, yes, he reveled in it. He was to the manner born.

As a scholar Hilgard belonged to and perhaps was the last prominent representative of the "naturalist" group of the last generation. And yet

he was beyond that generation since he specialized considerably. Trained successively as a chemist, geologist, and botanist, he gave the last forty years of his eventful life to the study of arid soils and their relations to plant growth. Beginning with his studies of the gases of the candle flame, upon which he wrote his doctor's dissertation, which was one of the bases of Bunsen's subsequent invention of the Bunsen burner, he evinced thus as early as 1853 that curiosity about Nature's unknown which grew in intensity with the years and rendered him an ever absorbed investigator and supporter of new research projects. I may digress to say that it was my good fortune to see the little pamphlet which was Hilgard's sole surviving copy of his doctor's thesis more than a half century after its publication and to discuss it with its author, who, as was customary and habitual with him on such occasions, gave me an hour of most charming reminiscences of Bunsen and other professors in Germany with whom he had worked. I recall particularly in that connection the characteristically delightful glee with which Hilgard told me of his final examination for the doctorate, in which the first question that Bunsen asked him was, "Herr Hilgard, was ist denn Methylalkohol?"

Unfortunately lack of space forbids my recounting here the long series of researches remarkable for their day which won Hilgard the distinguished position which history now accords him in the annals of science. Suffice it to say that whatever he touched he illuminated, and this was especially true in the field of soils, in which he was a pioneer, and to an understanding of which he was until recent years the most gifted contributor. His two hundred and fifty scientific papers, his two quarto volumes on the cotton investigations, published by the Census of 1880, and finally his celebrated book "Soils: Their Formation, Properties and Relations to Climate and Plant Growth in the Humid and Arid Regions", published in 1906, attest most eloquently his energy, clear-sightedness and ingenuity, as well as his charming literary style. The latter was made possible by his broad education and an inherent power of verbal expression, a combination possessed by few scientists. Whether or not the results of his investigations, particularly in his chosen field, remain a living and true picture of the subjects they sought to illuminate, is beside the point. The work of very few men in the history of all science, if indeed of any, stands authoritative, at least finally so today. It is no detraction, therefore, to say that most of Hilgard's results of experiments on physical and chemical soil problems, including his well-known experiments on alkali in soils and its relations with plant growth, stand now in question in the light of the stupendously rapid rise of more accurate investigations in chemistry and in plant physiology. The best established and oldest doctrines in science are even now giving way

before the remarkable discoveries of recent years, and even months, in the domains of physics and of physical chemistry. But let it not be supposed that this fact dims one whit the lasting value of the service rendered to science by those masterful scholars whose results formed the woof and warp of "modern" science for so long. Even so it is with Hilgard's work in his chosen field. His results were indispensable steps in the upward and progressive evolution of that branch of activity which is speedily establishing its right to be considered a science. Yea, they were not merely indispensable steps, they were bold, long, and numerous steps.

Thus in my humble way and in the most general terms I have tried to delineate the characteristics of Hilgard, the man, the teacher, the scholar, the leader. A thoroughly human, intellectual being, he was a grace to science and an ornament to society. He lived wisely, observed keenly, worked intensely, fought his battles bravely, loved and was beloved warmly, and died nobly. The manner in which he did all these things in the face of seemingly insurmountable obstacles through a very long, useful, and honored life must always be an inspiration to men. *Requiescat in pace.*

CHAS. B. LIPMAN.

GEORGE EDWARD PATRICK.

On March 22, 1916, after an illness that kept him from his office for only a few days, died Professor George Edward Patrick, M. Sc., Chief of the Dairy Laboratory of the Bureau of Chemistry, at the age of sixty-four years. Son of Delano and Mary (Maynard) Patrick, he was born October 22, 1851, at the Hopedale Community, founded by the Reverend Adin Ballou near Milford, Worcester County, Massachusetts.

After preparation in common and preparatory schools, the subject of this sketch entered Cornell University a few years after the opening of this institution, and was graduated with his bachelor's degree in 1873. The following college year he served there as assistant in organic and agricultural chemistry under Professor George Chapman Caldwell, one of the original members of the Association of Official Agricultural Chemists. At the same time, Mr. Patrick carried on post-graduate studies, and, upon the completion of the college year, received his degree of Master of Science from that university. Immediately thereafter, he became Assistant Professor of Chemistry at the University of Kansas, where he remained for a number of years, during which he succeeded to the full professorship in chemistry. There also, on June 19, 1879, he married Miss Hattie E. Lewis of that city. In 1883, having become

interested in metallurgy, he resigned his chair to accept the position of superintendent and manager of a mining and smelting company. Later he served as chemist to the Bradley Fertilizer Company of Boston. But in 1888, upon the organization of the Iowa Agricultural Experiment Station, Professor Patrick was asked to become its chemist, and in 1890 assumed the duties also of the Professor of Agricultural Chemistry in the college. The public demands upon the technical members of the experiment station staffs in the early days of those institutions prevented much specialization in the work of any of these officers. The bulletins of the Iowa station present many studies, individual or cooperative, by Professor Patrick upon the composition and nutritive values of various forage plants and other cattle feeds, upon the chemistry of the apple and the apple tree, and upon the sugar-producing qualities of sorghum and the sugar beet as grown in Iowa. The dominance of the dairy interests of the region soon led him to devote the major part of his laboratory effort to the chemical problems relating to that industry. He left the Iowa college and station in 1895. The following year Professor Patrick was appointed an assistant chemist under Dr. H. W. Wiley in the Department of Agriculture. Here he remained, devoting his attention exclusively to the examination of dairy products, and, upon the formation of the Dairy Laboratory of the Bureau of Chemistry, was made its Chief.

Professor Patrick was a master analyst of dairy products. We are indebted to him for a number of contributions to analytical methods and appliances. The use of the copper distillation flask in the determination of nitrogen by the Kjeldahl method was introduced by him. We owe to him the modification of the lactocrite method for the determination of fat in milk, a modification later known as the "brine test"; devices for the convenient sampling of milk and the measurement of acid for the Kjeldahl and Babcock methods; also, the perfecting of the Roese-Gottlieb method for fat determination in dairy products. This association is deeply indebted to him for numerous comparative studies upon the determination of various components and ingredients of milk products.

He was quiet in taste, did not seek the lime light, did not rush over-easily into print, and in the association meetings the frequency of his participation in debate fell far below the measure of his learning and experience. His judgments were formed carefully, expressed most positively, held tenaciously; yet his mind remained open to new truths. His generosity of character is beautifully illustrated by the hearty promptness with which he accepted and publicly commended the Babcock milk test upon its appearance just after, by several years of effort, the Patrick brine test had been perfected and brought into use; also by

his treatment of his assistants, of whom he nevertheless demanded painstaking accuracy. This generosity was balanced by a high sense of justice and courage. Domestic in tastes, spending his evenings at home, he was reluctant to assume duties which, for a time, separated him from his beloved wife. It was a source of deep grief to him that a long period of duty upon an important dairy investigation in the West had separated him from her for months prior to her death, which occurred in Denver during a brief reunion. This event shadowed all his remaining days.

WILLIAM FREAR.

THOMAS CUTHBERT TRESCOT.

I well remember the day in the summer of 1884 when T. C. Trescot first appeared in the old basement laboratory of the Chemical Division in the old red brick building of the Department of Agriculture. Born in Charleston, S. C., October 1, 1857, of a family possessing large landed interests but later impoverished in capital by the Civil War, he found it necessary to make his own way. His father, William Henry Trescot, lawyer and Assistant Secretary of State in the Confederate cabinet, was a man of high qualifications and great distinction. He attracted the attention of James G. Blaine during his term as Secretary of State, who sent him on a number of diplomatic missions requiring great skill and tact. He was accompanied on these missions by his son, Thomas Cuthbert. Trescot thus gained a wide knowledge of the world and its ways.

In the old days there was no Civil Service examination, and Trescot came to the old laboratory in the basement of the brick building where the Secretary of Agriculture still has his office, with a note from the Commissioner of Agriculture to Dr. Wiley to "put this boy to work". It was soon discovered that he had no knowledge of chemistry, but he had a great talent for work, and especially was he careful of all details of the work which were entrusted to him. Naturally, the work given him was of routine character, but he had a genius for routine. His knowledge of chemistry was never very much extended, but his knowledge of the best methods of determining nitrogen was perhaps not equalled by that of any other chemist in the world. He gave his whole service to that branch of chemical science. He began with the old soda-lime method, in which he became a master. This was followed by the old Ruffle method, in which he also became skilled. Then the moist composition process of Kjeldahl came into vogue. He knew that through all its variations of every description from beginning to end. He acquired a delicacy of technique, which was rarely secured by any other operator. By personality and craftsmanship he made his place, and when, with the

growth of the Bureau of Chemistry, a nitrogen laboratory was organized, he was made its chief. The members of this association who read with care its proceedings from the earliest days will appreciate how much we owe to Mr. Trescot's constant and careful aid in the cooperative study of the various nitrogen methods. What a unique experience—twenty-seven years of stirring life and seeing the world, and then thirty-two years in a little room making the same determination over and over again, and always with the steady aim of the craftsman at quality and quantity. But the cheeriness and the playful cynicism remained perennial, and always the self-respect without remotest tincture of self-conceit. In fact, I have always suspected that for Trescot the day up to 4.30 p. m. was the period of chores to be neatly and unfailingly performed, while the remaining hours were for real living, whether the life of the lover of sports and young clubman, or, in later days, when the right girl had come into his home, the life of the lover of the home hearth and of the proud father.

Mr. Trescot was married June 19, 1905, to Grace Matthews. Their daughter, Elizabeth Cuthbert, was born January 29, 1907. Their second daughter, Mildred Carlisle, was born May 4, 1911. Their son, Thomas Cuthbert, was born January 5, 1915. Trescot died April 14, 1916 from heart trouble.

Of his own ambitions he breathed no word, over his disappointments, was never heard to sigh; but let a comrade experience either joy or grief, and the shell of cynicism opened to let a warm heart peep almost shyly forth, and the voice that, but an instant before, had been joyously railing grew husky with sympathy. The esteem he won from his associates was manifested by a rare occurrence in departmental circles, a banquet celebrating the completion of his twenty-fifth year with the laboratory, an occasion shared by many professional friends widely scattered over the continent. I can not more fittingly close than by adopting the language of one of the toasts of that evening and dedicating this sketch to the memory of "a rare good friend, a man generous to a degree, ready always to help the under dog; in short, to a kindly, courteous South Carolina gentleman, whom it is good to have known".

WILLIAM FREAR.

Attention was called to the fact that the members of the Board of Editors were appointed originally for one, two, three, and four years, with the understanding that succeeding members were to be appointed for four years, and that a vacancy existed which had not been filled. A motion was made, seconded and duly adopted that the appointment of

members of the Board of Editors be referred to the Executive Committee with power to act.

Mr. H. C. Lythgoe moved that a rising vote of thanks be given to the president for the admirable manner in which he performed his duties. The motion was unanimously carried.

It was moved, seconded and adopted that the next meeting be held in Washington, D. C., and, if possible, at the New Willard.

The convention adjourned.

UNIVERSITY OF CALIFORNIA
LIBRARY

INDEX TO VOLUME III

PROCEEDINGS OF THE FIRST AFTERNOON AND LAST TWO DAYS OF THE THIRTY-SECOND ANNUAL CONVENTION, 1915, AND OF THE THIRTY-THIRD ANNUAL CONVENTION, 1916.

PAGE

Acidity, titration in colored solutions, paper by Hartmann 410
Acid soils, lime requirements, paper by Conner 139
Address
  by Vrooman, Acting Secretary of Agriculture 418
  of Honorary President, by Wiley 420
Adulteration, food, report by Hortvet 398
Alcohol tables, paper by St. John, reference 197
Alkaloids
  recommendations by Fuller 193, 380
  report by Fuller 188, 379
Alsberg
  financial statement, Journal 576
  report
    of Secretary-Treasurer
      for year ending November 17, 1915 54
      for year ending November 22, 1916 576
    on Journal 55
Alternative method, defined 227
Amendments to constitution and by-laws, report of committee (Ross) 586
Ames, report, soils 121
Amino acids and grain extracts in presence of alcohol, acidimetric titration, paper by Birckner, reference 255
Ammonia
  determination in fertilizers, substitution of sodium sulphate for potassium sulphate in Kjeldahl-Gunning-Arnold method, paper by Jarrell 304
  retention, relation of lime requirements of soils, paper by Howard, reference 374
Animal tissue, inorganic phosphorus content, report
  by Beegle 204
  by Forbes 264
Arsenic, C. R. Smith's method for determination, paper by Collins, reference 518
Arsenic pentoxid and arsenic trioxid, occurrence and determination in arsenical insecticides, paper by Roark 358
Associate referees, officers, referees, and committees, for year ending November 1917 228
Attendance at 1916 convention 231
Auditing committee
  appointment and personnel 53, 279
  report 577

Bacteriological examination of foodstuffs, proposed committee, paper by Thom, reference 203
Baking powder
  changes in methods 572
  recommendations
    by Committee C 85, 536
    by Patten 432
  report by Patten 429
Balcom, paper
  calculation of volume of liquid from weight and specific gravity 413
  volatile reducing substance in cider vinegar, reference 415
Balcom and Grab, paper, isolation and identification of glycerol in cider vinegar .. 411
Balsam Peru
  preliminary study of physical and chemical constants, report by Merrill 194
  recommendations by Merrill 197

PAGE

Barnard, report of Committee C on recommendations of referees and revision of methods....72, 528
Bartlett, report, tea and coffee.... 21
Basic slag
availability of phosphoric acid, report by committee (Williams) 104, 585
phosphoric acid content
recommendations by Lykes.... 288
report by Lykes.... 286
recommendations by Walker.... 96
Beegle, report, inorganic phosphorus in animal tissue.... 204
Beers
changes in methods.... 561
recommendations by Committee C.... 84
Benzaldehyde, manufacture with benzoic acid as a by-product, paper by Gibbs and Geiger, reference.... 512
Benzoic acid, by-product in manufacture of benzaldehyde, paper by Gibbs and Geiger, reference.... 512
Bigelow, report, canned vegetables....1, 453
Birckner, paper
acidimetric titration of grain extracts and amino acids in presence of alcohol, reference.... 255
simple method for measuring acidity of cereal products; application to sulphured and unsulphured oats, reference.... 255
Bloomberg, report, cocoa and cocoa products.... 486
Bones and tankage, recommendation by Walker.... 96
Bosworth, report, separation of nitrogenous substances (milk and cheese).... 53
Brackett, President's address.... 238
Brackett and Haskins, report, nitrogen.... 207
Browne, report, sugar.... 261
Buc, paper
delicate test for strychnin.... 193
estimation of strychnin in presence of quinin, reference.... 193
By-laws and constitution, amendments, report of committee (Ross).... 586

Cacao products
changes in methods.... 571
See also Cocoa and cocoa products.
Canned vegetables. *See* Vegetables, canned.
Cereal products
changes in methods.... 558
method for measuring acidity; application to sulphured and unsulphured oats, paper by Birckner, reference.... 255
recommendations
by Committee C....87, 532
by Le Clerc.... 451
report by Le Clerc.... 446
Cheese and milk, separation of nitrogenous substances
recommendation
by Bosworth.... 53
by Committee B.... 71
by Palmer.... 274
report
by Bosworth.... 53
by Palmer.... 273
Chemical reagents, testing
recommendations
by Committee B....71, 528
by Ewing....226, 277
report by Ewing....225, 276
Chesnut
paper, determination of pepsin in liquids, reference.... 197
report, papain.... 387
Cider, changes during fermentation, storage, and conversion into vinegar, paper by Hartmann and Tolman, reference.... 415

PAGE

Citrates, use in determination of phosphoric acid, report by Jones 97
Cocoa and cocoa products
changes in methods 571
recommendations
by Bloomberg 497
by Committee C 535
report by Bloomberg 486
Coffee and tea
adoption of methods 571
recommendations
by Bartlett 24
by Committee C 87, 536
by Loomis 503
report
by Bartlett 21
by Loomis 498
Collins, paper, C. R. Smith's method for determination of arsenic, reference 518
Colors
changes in methods 555
recommendations by Committee C 72
report, Mathewson 400
tartrazine, paper by Doyle 402
Committee A on recommendations of referees and revision of methods, report (Skinner) 59, 519
Committee B on recommendations of referees and revision of methods, report (Stallings) 66, 524
Committee C on recommendations of referees and revision of methods, report (Barnard) 72, 528
Committee of review on analysis of lime sulphur solutions, report (Davidson) 188
Committee on amendments to constitution and by-laws, report (Ross) 586
Committee on auditing
appointment and personnel 53, 279
report 577
Committee on availability of phosphoric acid in basic slag, report (Williams) 104, 585
Committee on editing methods of analysis, report (Doolittle) 89, 537
Committe on food definitions and standards, report (Frear) 198, 580
Committee on nominations
appointment and personnel 53, 279
report (Ellett) 187
report (McDonnell) 589
Committee on resolutions
appointment and personnel 53, 279
report (Davidson) 187
report (Frear) 589
Committee to invite Secretary of Agriculture to address convention, appointment and personnel 279
Committees, appointment and personnel 53, 279
Committees, officers, referees, and associate referees, for year ending November 1917 228
Condiments
changes in methods 569
recommendations by Committee C 535
Conner, paper, lime requirements of some acid soils 139
Constitution and by-laws, amendments, report of committee (Ross) 586
Cottonseed meal, inosite-phosphoric acids, paper by Rather, reference 254
Crude fiber
recommendations
by Committee B 525
by Francis 260
report by Francis 256
Cutler, report, feed adulteration 255

Dairy products
changes in methods 568

PAGE

recommendations
by Committee B....66, 526
by Committee C....87, 534
by Hortvet....446
by Klueter....254
report
by Hortvet....436
by Klueter....254
Daudt and Phelps, report, investigations of Kjeldahl method for determination of nitrogen....218, 306
Davidson, report
of committee of review on analysis of lime sulphur solutions....188
of committee on resolutions....187
Davidson, Robert James, obituary by Ellett....591
Deemer, report, nitrogen determination....299
Distilled liquors, changes in methods....560
Doolittle, report of committee on editing methods of analysis....89, 537
Doyle, paper, tartrazine....402
Drugs
changes in methods....572
emodin-bearing, identification, paper by Hubbard, reference....197
recommendations by Committee B....71, 527
Dunbar and Lepper, report, fruit products....402

Editing methods of analysis, report of committee (Doolittle)....89, 537
Edmiston, Frear, and Thomas, paper, use of potassium permanganate in determining nitrogen by Kjeldahl method....220
Emodin-bearing drugs, identification, paper by Hubbard, reference....197
Ellett
obituary on Robert James Davidson....591
report of committee on nominations....187
Emery, report, synthetic products....374
Ether, new method for drying, paper by West....101
Ewing, report, testing chemical reagents....225, 276
Extracts, flavoring
changes in methods....562
recommendations
by Committee C....84, 533
by Paul....416
report by Paul....415

Fats and oils
changes in methods....568
recommendations
by Committee C....86, 535
by Kerr....436
report by Kerr....432
Feed adulteration
recommendations
by Committee B....525
by Cutler....256
report by Cutler....255
Feeding stuffs and foods
changes in methods....551
recommendations by Committee B....67, 524
report by Summers....254
Fertilizers
changes in methods....538
determination
of ammonia, substitution of sodium sulphate for potassium sulphate in Kjeldahl-Gunning-Arnold method, paper by Jarrell....304
of nitrogen, paper by Trowbridge....217
Fiber, crude. *See* Crude fiber.

PAGE

Fish and meat, recommendations by Committee C 86
Flavoring extracts. *See* Extracts, flavoring.
Food adulteration, report by Hortvet 398
Foods and feeding stuffs
  changes in methods 551
  organic and inorganic phosphorus content, recommendations by Committee B 70
  recommendations by Committee B 67, 524
  report by Summers 254
  water content
    recommendations by Committee B 70
    report by McGee 264
Foodstuffs, bacteriological examination, paper by Thom, reference 203
Forbes, report, inorganic phosphorus in animal tissue 264
Francis, report, crude fiber 256
Frear
  obituary
    on George Edward Patrick 596
    on Thomas Cuthbert Trescot 598
  report
    of committee on food definitions and standards 198, 580
    of committee on resolutions 589
Frear, Thomas, and Edmiston, paper, use of potassium permanganate in determining nitrogen by Kjeldahl method 220
Fruit and fruit products
  changes in methods 557
  recommendations
    by Committee C 84, 530
    by Dunbar and Lepper 409
  report by Dunbar and Lepper 402
Fuller, report, alkaloids 188, 379
Fungicides and insecticides
  changes in methods 548
  recommendations by Committee A 62, 521

Geiger and Gibbs, paper, manufacture of benzaldehyde with benzoic acid as a by-product, reference 512
Gibbs and Geiger, paper, manufacture of benzaldehyde with benzoic acid as a by-product, reference 512
Glycerol
  calculation of volume of liquid from weight and specific gravity, paper by Balcom 413
  isolation and identification in cider vinegar, paper by Balcom and Grab 411
Gnadinger, paper, determination of saccharin in foods 25
Grab and Balcom, paper, isolation and identification of glycerol in cider vinegar 411
Grain extracts and amino acids in presence of alcohol, acidimetric titration, paper by Birckner, reference 255

Hartmann
  paper, titration of acidity in colored solutions 410
  report, wine 409
Hartmann and Tolman, paper, vinegar investigation, changes cider undergoes during fermentation and prolonged storage, and subsequent conversion into vinegar in rotating generators, reference 415
Haskins, report, nitrogen 289
Haskins and Brackett, report, nitrogen 207
Hilgard, Eugene Woldemar, obituary by Lipman 592
Horne, recommendations, sugar 263
Hortvet, report
  dairy products 436
  food adulteration 398

PAGE

Howard, paper
determination of lime requirements of soils by use of calcium bicarbonate.... 141
relation of lime requirements of soils to their retention of ammonia, reference 374
Hubbard, paper, identification of emodin-bearing drugs, reference..... 197
Hudson, representative, Pan-American Scientific Congress..... 53

Inorganic phosphorus in animal tissue
recommendations by Forbes..... 273
report by Forbes..... 264
Inorganic plant constituents
recommendations
by Committee A.....61, 521
by Patten.....156, 331
report by Patten.....153, 329
Inosite-phosphoric acids of cottonseed meal, paper by Rather, reference..... 254
Insecticides
arsenical, As^{III} and As^{V} content, paper by Roark..... 358
recommendations
by Committee A.....62, 521
by Roark.....185, 357
report by Roark.....157, 331
Insecticides and fungicides
changes in methods..... 548
recommendations by Committee A.....62, 521

Jarrell
paper, substitution of sodium sulphate for potassium sulphate in Kjeldahl-Gunning-Arnold method for determination of ammonia in fertilizers..... 304
report
determination of potash.....107, 315
Jones, report
phosphoric acid..... 279
use of citrates in determination of phosphoric acid..... 97
Journal
financial statement (Alsberg).....54, 576
report by Alsberg.....55, 578

Keitt and King, paper, new, rapid and accurate method for estimating lime and potash in soils, reference..... 326
Kerr, report, fats and oils..... 432
King and Keitt, paper, new, rapid and accurate method for estimating lime and potash in soils, reference..... 326
Kjeldahl-Gunning-Arnold method for determination of ammonia in fertilizers, substitution of sodium sulphate for potassium sulphate, paper by Jarrell..... 304
Kjeldahl method for determination of nitrogen
report
by Phelps and Daudt.....218, 306
use of potassium permanganate, paper by Frear, Thomas, and Edmiston.... 220
Klein, report, metals in food..... 512
Klueter, report, dairy products..... 254
Kuzirian, paper, separation and gravimetric estimation of potassium..... 321

Leathers, changes in methods..... 548
Le Clerc, report, cereal products..... 446
Lepper and Dunbar, report, fruit products..... 402
Lime and potash in soils, new, rapid and accurate method for estimation, paper by Keitt and King, reference..... 326
Lime requirement
of soils
determination, by use of calcium bicarbonate, paper by Howard..... 141
relation to retention of ammonia, paper by Howard, reference..... 374
report by Veitch..... 371

PAGE

of some acid soils, paper by Conner ... 139
status of problem, paper by McIntire ... 144
Limestone, residual, soil containing, paper by Noyes ... 151
Lime sulphur solutions, committee of review on analysis, report (Davidson) ... 188
Lipman
obituary on Eugene Woldemar Hilgard ... 592
report, nitrogenous compounds in soils ... 326
Liquors, distilled, changes in methods ... 560
Loomis, report, tea and coffee ... 498
Lykes, report, phosphoric acid in basic slag ... 286

Mathewson, report, colors ... 400
McDonnell, report of committee on nominations ... 589
McGee, report, water in foods and feeding stuffs ... 264
McIntire, paper, status of problem of lime requirement ... 144
Meat and fish, recommendations by Committee C ... 86
Meat and meat products
changes in methods ... 563
recommendations by Trowbridge ... 580
Meat products, separation of nitrogenous substances
recommendations
by Committee B ... 71, 527
by Trowbridge ... 276
report by Trowbridge ... 275
Medicinal plants
recommendations by Viehoever ... 386
report by Viehoever ... 381
Medicinal plants and drugs, recommendations by Committee B ... 71, 527
Members and visitors at 1916 convention ... 231
Merrill, report, preliminary study of physical and chemical constants of balsam Peru ... 194
Metals
C. R. Smith's method for determination of arsenic, paper by Collins, reference 518
in foods
changes in methods ... 556
recommendations
by Committee C ... 88, 530
by Klein ... 518
by Treuthardt ... 52
report
by Klein ... 512
by Treuthardt ... 43
Methods
alternative, optional, and provisional defined ... 227
designated by names of authors ... 575
of analysis, report of committee on editing (Doolittle) ... 89, 537
Milk and cheese, separation of nitrogenous substances
recommendation
by Bosworth ... 53
by Committee B ... 71, 527
by Palmer ... 274
report
by Bosworth ... 53
by Palmer ... 273
Milk, cows', neutralization precipitate, paper by Palmer ... 274

Nitrogen
determination
in fertilizers, paper by Trowbridge ... 217
investigations of Kjeldahl method, report
by Phelps and Daudt ... 218, 306
recommendations by Deemer ... 304

PAGE
report by Deemer ... 299
use of potassium permanganate in Kjeldahl method, paper by Frear, Thomas, and Edmiston ... 220
recommendations
by Brackett and Haskins ... 217
by Committee A ... 61, 520
report
by Brackett and Haskins ... 207
by Haskins ... 289
Nitrogenous compounds in soils
recommendations by Lipman ... 328
report by Lipman ... 326
Nitrogenous substances, separation
meat products
recommendation
by Committee B ... 71, 527
by Trowbridge ... 276
report by Trowbridge ... 275
milk and cheese
recommendation
by Bosworth ... 53
by Committee B ... 71, 527
by Palmer ... 274
report
by Bosworth ... 53
by Palmer ... 273
Nominations
committee, appointment and personnel ... 53, 279
report of committee (Ellett) ... 187
report of committee (McDonnell) ... 589
Noyes, paper
determination of phosphorus in soils ... 149
study of soil containing residual limestone ... 151

Oats, sulphured and unsulphured; method for measuring acidity of cereal products, paper by Birckner, reference ... 255
Officers, referees, associate referees, and committees for year ending November 1917 ... 228
Oils and fats
changes in methods ... 568
recommendations
by Committee C ... 86, 535
by Kerr ... 436
report by Kerr ... 432
Optional method, defined ... 227

Palmer
paper, origin of neutralization precipitate of cows' milk ... 274
report, separation of nitrogenous substances in milk and cheese ... 273
Pan-American Scientific Congress, representatives named ... 53
Papain, report by Chesnut ... 387
Patrick, George Edward, obituary by Frear ... 596
Patten, A. J., report, inorganic plant constituents ... 153, 329
Patten, H. E., report, baking powder ... 429
Paul, report, flavoring extracts ... 415
Pepsin in liquids, determination, paper by Chesnut, reference ... 197
Peru balsam. *See* Balsam Peru.
Phelps and Daudt, report, investigations of Kjeldahl method for determination of nitrogen ... 218, 306
Phosphoric acid
recommendations
by Committee A ... 59, 519
by Jones ... 286
by Walker ... 95, 96

PAGE

report
by Jones ... 279
by Walker ... 90
use of citrates in determination, report by Jones ... 97
Phosphoric acid and potash, preparation of organic material for determination in aliquots of same solution, paper by West ... 99
Phosphoric acid, availability in basic slag, report of committee (Williams) ... 104, 585
Phosphoric acid in basic slag
recommendations by Lykes ... 288
report by Lykes ... 286
Phosphorus
inorganic
in animal tissue
recommendations by Forbes ... 273
report
by Beegle ... 204
by Forbes ... 264
in soils, determination, paper by Noyes ... 149
organic and inorganic, recommendations by Committee B ... 70, 526
Plant constituents
changes in methods ... 544
inorganic
recommendations
by Committee A ... 61, 521
by Patten ... 156, 331
report, by Patten ... 153, 329
Plants and drugs, medicinal
recommendation by Committee B ... 71, 527
recommendations by Viehoever ... 386
report by Viehoever ... 381
Potash
availability
in commercial wood ashes, paper
by Rose ... 323
by Stallings and Wilson, reference ... 323
report by Vanatta ... 105
recommendations
by Committee A ... 60, 520
by Jarrell ... 121, 321
report by Jarrell ... 107, 315
Potash and lime in soils, new, rapid and accurate method for estimation, paper by Keitt and King, reference ... 326
Potash and phosphoric acid, preparation of organic material for determination in aliquots of same solution, paper by West ... 99
Potassium permanganate, use in determining nitrogen by Kjeldahl method, paper by Frear, Thomas, and Edmiston ... 220
Potassium, separation and gravimetric estimation
paper by Kuzirian ... 321
recommendations by Kuzirian ... 323
Potassium sulphate, substitution of sodium sulphate in Kjeldahl-Gunning-Arnold method for determination of ammonia in fertilizers, paper by Jarrell ... 304
Preservatives, food
changes in methods ... 554
recommendations
by Committee C ... 88, 528
by Seeker ... 38, 511, 512
by Seeker and Wolf ... 42
report by Seeker ... 33, 504
President's address by Brackett ... 238
Provisional method, defined ... 227

PAGE

Quinin, estimation of strychnin in presence, paper by Buc, reference 193

Rather, paper, inosite-phosphoric acids of cottonseed meal, reference 254
Reagents, chemical, testing
recommendations
by Committee B 71, 528
by Ewing 226, 277
report by Ewing 225, 276
Recommendations of referees and revision of methods, report
of Committee A (Skinner) 59, 519
of Committee B (Stallings) 66, 524
of Committee C (Barnard) 72, 528
Referees, distribution revised 579
Referees, officers, associate referees, and committees, for year ending November 1917. 228
Resolutions
committee, appointment and personnel 53, 279
report of committee (Davidson) 187
report of committee (Frear) 589
Roark
paper, occurrence and determination of As^{III} and As^{V} in presence of each other in arsenical insecticides 358
report, insecticides 157, 331
Rose, paper, availability of potash in commercial wood ashes 323
Ross, report of committee on amendments to constitution and by-laws 586

Saccharine products
changes in methods 553
recommendations by Committee C 84
Saccharin in foods, determination, report by Gnadinger 25
Secretary-Treasurer, report
for year ending November 17, 1915 (Alsberg) 54
for year ending November 22, 1916 (Alsberg) 576
Seeker, report, preservatives 33, 504
Sindall, report, spices 427
Skinner, report
of Committee A on recommendations of referees and revision of methods 59, 519
water 368
Slag, basic
availability of phosphoric acid, report of committee (Williams) 104, 585
recommendations by Walker 96
Slag, Thomas. *See* Slag, basic.
Smith, C. R., method for determination of arsenic, paper by Collins, reference 518
Sodium sulphate, substitution for potassium sulphate in Kjeldahl-Gunning-Arnold method for determination of ammonia in fertilizers, paper by Jarrell 304
Soil containing residual limestone, paper by Noyes 151
Soils
acid, lime requirement, paper by Conner 139
changes in methods 541
determination of phosphorus, paper by Noyes 149
lime and potash estimation, new, rapid and accurate method, paper by Keitt and King, reference 326
lime requirement
determination by calcium bicarbonate, paper by Howard 141
relation to retention of ammonia, paper by Howard, reference 374
report by Veitch 371
status of problem, paper by McIntire 144
nitrogenous compounds
recommendations by Lipman 328
report by Lipman 326
recommendations
by Ames 138
by Committee A 60, 520
report by Ames 121

PAGE

Specific gravity and weight, calculation of volume of liquid, paper by Balcom.... 413
Spices and other condiments
changes in methods 569
recommendations
by Committee C.....85, 535
by Sindall..... 428
report by Sindall..... 427
Stallings, report of Committee B on recommendations of referees and revision of methods.....66, 524
Stallings and Wilson, paper, availability of potash in wood ashes, reference..... 323
Standards and definitions, report of committee (Frear).....198, 580
St. John, paper, alcohol tables, reference..... 197
Stock feed adulteration, recommendations by Committee B..... 525
Strychnin
delicate test, paper by Buc..... 193
estimation in presence of quinin, paper by Buc, reference..... 193
Sugar
recommendations
by Browne..... 263
by Committee B.....67, 525
by Horne..... 263
report by Browne..... 261
Summers, report, foods and feeding stuffs..... 254
Synthetic products, report by Emery..... 374

Tankage and bones, recommendation by Walker..... 96
Tanning materials, changes in methods..... 546
Tartrazine, paper by Doyle..... 402
Tea and coffee
adoption of methods..... 571
recommendations
by Bartlett..... 24
by Committee C.....87, 536
by Loomis..... 503
report
by Bartlett..... 21
by Loomis..... 498
Thom, paper, proposed committee on bacteriological examination of foodstuffs, reference..... 203
Thomas, Frear, and Edmiston, paper, use of potassium permanganate in determining nitrogen by Kjeldahl method..... 220
Thomas, slag. *See* Basic slag.
Titration, acidimetric, grain extracts and amino acids in presence of alcohol, paper by Birckner, reference..... 255
Tolman and Hartmann, paper, vinegar investigation, changes cider undergoes during fermentation and prolonged storage, and subsequent conversion into vinegar in rotating generators, reference..... 415
Treasurer, report
for year ending November 17, 1915 (Alsberg)..... 54
for year ending November 22, 1916 (Alsberg)..... 576
Trescot, Thomas Cuthbert, obituary by Frear..... 598
Treuthardt, report, heavy metals in foods..... 43
Trowbridge
paper, determination of nitrogen in fertilizers..... 217
recommendations, meat and meat products..... 580
report, separation of nitrogenous substances in meat products..... 275

Vanatta, report, availability of potash..... 105
Vegetables, canned
changes in methods..... 557
recommendations by Committee C..... 530
report by Bigelow.....1, 453
Veitch, report, lime requirement of soils..... 371
Viehoever, report, medicinal plants..... 381

PAGE

Vinegar
calculation of volume of liquid from weight and specific gravity, paper by Balcom ... 413
changes in cider during fermentation, storage, and conversion into vinegar, paper by Hartmann and Tolman, reference ... 415
changes in methods ... 562
cider
isolation and identification of glycerol, paper by Balcom and Grab ... 411
volatile reducing substance, paper by Balcom, reference ... 415
Vrooman, address as Acting Secretary of Agriculture ... 418

Walker, report, phosphoric acid ... 90
Water
changes in methods ... 544
in foods and feeding stuffs
recommendations by Committee B ... 70
report by McGee ... 264
recommendations
by Committee A ... 65, 522
by Committee B ... 526
by Skinner ... 371
report by Skinner ... 368
West, paper
new method for drying ether and sample in determination of ether extract ... 101
preparation of organic material for determination of phosphoric acid and potash in aliquots of same solution ... 99
Wiley
Honorary President's address ... 420
representative, Pan-American Scientific Congress ... 53
Williams, report of committee on availability of phosphoric acid in basic slag 104, 585
Wilson and Stallings, paper, availability of potash in wood ashes, reference ... 323
Wines
changes in methods ... 559
recommendations by Committee C ... 84, 532
report by Hartmann ... 409
titration of acidity in colored solutions, paper by Hartmann ... 410

JOURNAL

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

Vol. III MAY 15, 1920 No. 4

BOARD OF EDITORS

C. L. Alsberg, Chairman

R. E. Doolittle C. B. Lipman

E. F. Ladd L. L. Van Slyke

N. A. Parkinson, Associate Editor

Proceedings of the Thirty-third Annual Convention, held at Washington, D. C., November 20–22, 1916

Tuesday Afternoon Session

Wednesday Morning Session

Wednesday Afternoon Session

PUBLISHED QUARTERLY BY
THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS
BOX 744, ELEVENTH STREET STATION,
WASHINGTON, D. C.

Copyright, 1920, by Association of Official Agricultural Chemists
Application pending for entry as Second Class Matter at Washington, D. C.

SPECIALTIES
FOR FERTILIZER LABORATORIES

IN OUR STOCK FOR IMMEDIATE SHIPMENT

POTASSIUM SULPHATE

POTASSIUM SULPHATE, "Kjelgest" Brand, a pure grade of Potassium Sulphate, practically free from nitrogen (not over .01% blank when using 10 grams when calculated on a basis of 1.7034 grams of sample), containing less than 2% moisture; entirely satisfactory for making digestions for the determination of nitrogen by the official methods of the Association of Official Agricultural Chemists.

Per lb. in 5 lb. paper lined boxes ..... **$ .50**
Per lb. " 10 lb. " " " ..... **.40**
Per lb. " 200 lb. bags ..... **.30**

MANNITE

MANNITE, as used for the determination of borax.

Per lb. in 1 lb. cartons **$6.50**

VOLUMETRIC FLASKS

No. 28325

28325. FLASKS, VOLUMETRIC, PHOSPHORIC ACID, 200 ml. capacity, for the determination of insoluble phosphoric acid; made of heavy glass to withstand violent shaking, and with 200 ml. mark low on neck. As used in the Massachusetts Agricultural Experiment Station ..... **$ .70**

10% discount in carton containing 12
20% " " case " 144

No. 28328

28328. FLASKS, VOLUMETRIC, FERTILIZER, 250 ml. capacity, with short neck and with mark low on neck; of heavier glass than regular volumetric flasks ..... **$ .65**

10% discount in case containing 72

Prices subject to change without notice.

ARTHUR H. THOMAS COMPANY

WHOLESALE, RETAIL AND EXPORT MERCHANTS

LABORATORY APPARATUS AND REAGENTS

WEST WASHINGTON SQUARE — PHILADELPHIA, U. S. A.

Made For Chemists By Chemists

Among the great family of R.I.W. Products, there are a number which appeal particularly to the chemical industry—

R.I.W. ACID-PROOF PAINTS

Preserve steel and other surfaces against acid and alkali fumes, electrolytic and chemical corrosion, water and steam.

For use on pipes, benches, machines, in laboratories, storage battery rooms, plating works, storage battery rooms, etc.

R.I.W. HOSPITAL & LABORATORY ENAMEL

A white enamel that resists the action of sulphuretted hydrogen, gases and fumes of acids and chemicals. A three coat enamel that positively does not turn color. High gloss, matt or egg-shell finish as desired.

R.I.W. CEMENT FILLER & CEMENT FLOOR PAINT

Preserve and decorate concrete floors and render them wear-proof, oil-proof and water-proof. Cement Filler binds the surface into a hard, homogeneous mass and stops "cement dusting." Cement Floor Paint as a finisher imparts any standard color and makes a better wearing surface.

R.I.W. TOXEMENT

A powder to add to Portland Cement at the mixing to make cement construction thoroughly water-proof. Doesn't hasten or retard setting action, but lubricates the mass, binding it into a denser and more impenetrable body.

Full details of these and other preservatives for the chemical industries in "The Red Book" from Dept. 30

TOCH BROTHERS

TECHNICAL AND SCIENTIFIC PAINT MAKERS SINCE 1848

320 FIFTH AVE., NEW YORK

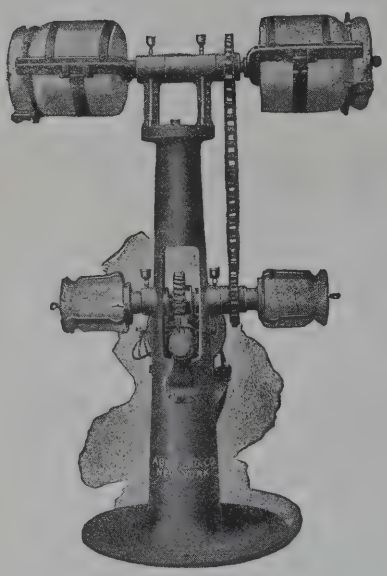
WORKS: LONG ISLAND CITY, N. Y. AND LONDON, ENGLAND

R.I.W. REMEMBER IT'S WATERPROOF REG. U.S. PAT. OFF.

STEEL NEED NOT RUST!
WOOD NEED NOT ROT!
NOR CONCRETE DUST!

ABBÉ

PULVERIZING MACHINERY



Combination Laboratory Mill
We Build this with any Combination of Different Size Jars

BETTER CRUSHING AND GRINDING AT LOWER COST

OUR VARIOUS MACHINES ARE UNIVERSALLY RECOGNIZED AS THE STANDARD FOR LABORATORY AND COMMERCIAL USE

When you purchase Abbé Equipment it is not simply a case of buying a Ball or Pebble Mill, a Cutter, Crusher, Pressure Blower or Vacuum Pump. It is a case of getting the result of conscientious Engineering Service based on **39** years of experience in this field. If you are looking for large capacity, low power consumption, continuous operation—in short, for SATISFACTION—investigate ABBÉ Equipment.

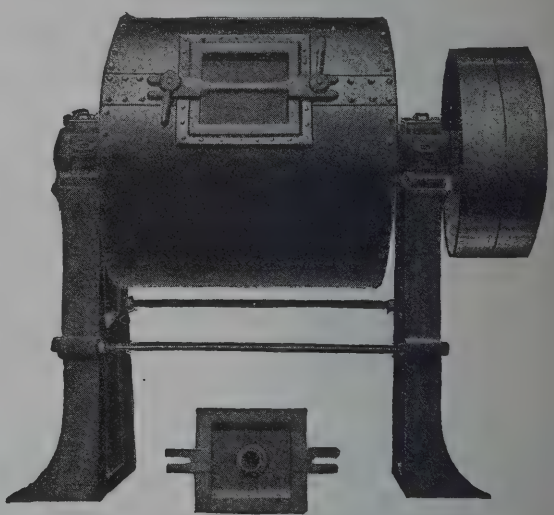
USE OUR TESTING LABORATORY

We make no charge for grinding, crushing, cutting or mixing samples and submitting full reports on suitable machines. We operate a considerable number of different mills for this purpose. Get in touch with us.

ABBÉ PRODUCTS

LABORATORY MILLS
JAR MILLS
PEBBLE MILLS
BALL MILLS
TUBE MILLS
DISINTEGRATORS
ROTARY CUTTERS
VACUUM PUMPS
PRESSURE BLOWERS
BOLTING CLOTH

OVER 100 MACHINES IN STOCK

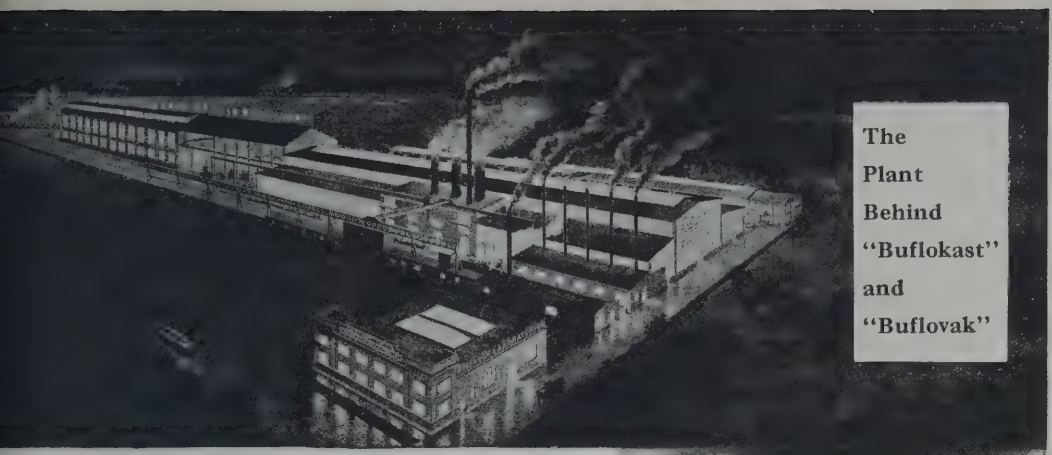


Abbé Pebble Mill
(Patented)
For Wet or Dry Grinding, for Charging Capacities up to 4,000 Pounds, Lined with either Silex, Porcelain, Cast Iron or Steel

SEND FOR CATALOGS

ABBÉ ENGINEERING CO.

1109 ST. PAUL BLDG. **NEW YORK**



The Plant Behind "Buflokast" and "Buflovak"

"Buflokast" Chemical Apparatus

"Buflovak" Vacuum Dryers

"Buflovak" Evaporators

"Buflovak" Sugar Mill Machinery

TRADE NAMES WHICH SIGNIFY HIGH QUALITY

Distinguishing names are given to our various products so that they may at all times be instantly recognized from ordinary apparatus.

The superior performance of "Buflovak" and "Buflokast" apparatus in manufacturing high quality products at low production costs in innumerable instances warrants these special designations. This superiority is not the result of accident, but the outcome of scientific research and knowledge acquired by years of experience in manufacturing successful apparatus used by the foremost manufacturers of the world.

CATALOG MAILED ON REQUEST

Buffalo Foundry & Machine Co.

7 Winchester Avenue BUFFALO, N. Y.

New York Office: 17 Battery Place

Attention Chemists!

New Book!

Official
and
Tentative Methods
of
Analysis
of the
Association of Official Agricultural Chemists

Revised to November 1, 1919

Approximately 400 pages. Size of page 6 x 9 inches. Printed on a high grade rag paper. Bound in library buckram. Price $5.00. Will appear about August 15th.

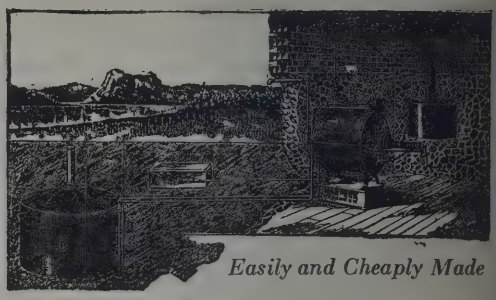
Published by

The Association of Official Agricultural Chemists

Box 744, Eleventh Street Station

Washington, D. C.

GAS— A Modern Necessity



Easily and Cheaply Made

For ALL Heating Purposes

Unequalled for the Laboratory and all Branches of Chemistry

A standard, uniform, non-poisonous gas, absolutely safe, simple and efficient, supplied automatically as wanted by the

TIRRILL
Equalizing
Gas Machine

Fully guaranteed; easily installed. Nothing to get out of order. Does not affect insurance rates.

Tirrill High Efficiency Burners

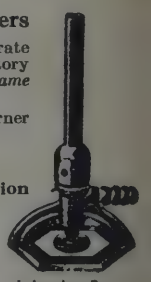
Used for over 50 years and found superor in every respect.

Scientifically constructed. Guaranteed to work on all kinds of gas, under any pressure. So constructed that the air and gas regulator cannot become hot while the burners are in use. TIRRILL Burners insure a gas saving of 25 to 50%.

TIRRILL Laboratory Burners

Burner illustrated is made with separate air and gas adjustment. Other laboratory burners regulate air and gas at the *same* time.

TIRRILL Blast Flame Heating Burner No. 2000 will deliver 2000 heat units.



Laboratory Burner

A Burner for Every Need

The famous TIRRILL Combination Mixing Valve for properly regulating air and gas, is unexcelled for hot-plates, stills, sterilizers, autoclaves, warming closets, blast furnaces, gas fuel heating appliances, ovens, water heaters and ranges.

Also Fuel Gas Plants, Gasoline, Underground Storage Tanks, Sheet-Metal Work, etc.

BOOKLET UPON REQUEST

TIRRILL GAS MACHINE LIGHTING CO.

Established 1864

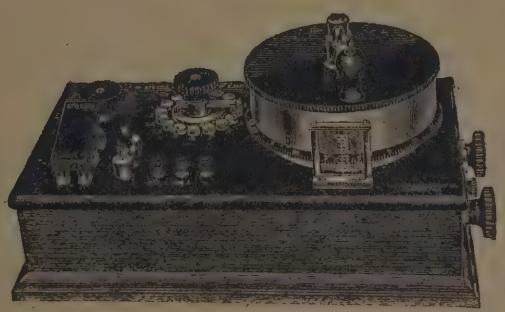
614 Terminal Bldg., 103 Park Ave., New York City

WHAT DOES P_H MEAN?

The symbol P_H is an index of the acidity or basicity—in other words, of the concentration of the hydrogen ions—in a solution. The frequent occurrence of references to this important quantity in current scientific literature is an index of its growing importance in the chemical and biological sciences.

Since hydrogen ion concentration of culture media, body fluids and of other solutions has great significance, it is important that its value be accurately measurable.

Color, turbidity, light conditions, or the formation of precipitates should not interfere with the measurement. The result should be **actual acidity,** unmodified by a titrating solution. The means for making the measurement should be capable of quick and simple operation.



The Type K Potentiometer Outfit fully meets these demands. It does more—it has additional features which make it invaluable in the up-to-date research or control laboratory. It measures the entire range of acidity, from $P_H = O$ to $P_H = 14$. The accuracy is better than 0.01 P_H, and this is limited only by the reproducibility of experimental conditions in the medium.

Our circular Q70 with its supplement 701 gives interesting information about the Type K equipment. These, together with a bibliography of articles on electrometric hydrogen ion determinations, we shall gladly send you upon request.

LEEDS & NORTHRUP COMPANY

ELECTRICAL MEASURING INSTRUMENTS

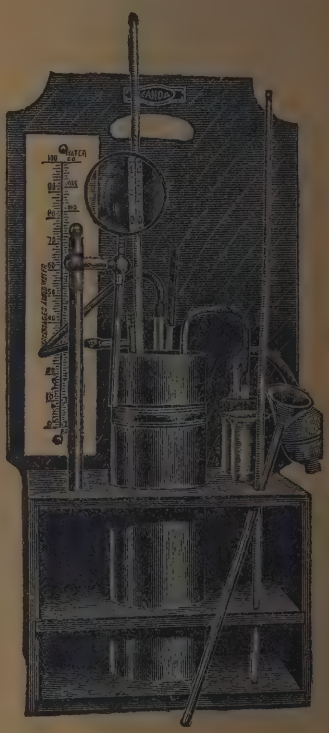
4901 STENTON AVE. **PHILADELPHIA, PA.**

The Hortvet Cryoscope

An Instrument for Determining the Freezing-Point of Milk

THE CRYOSCOPIC TEST

No other chemical or physical property of whole milk is so fundamental and uniform as the freezing-point, and therefore this test is of extremely great importance in the routine examination of samples of market milk.



USES OF THE HORTVET CRYOSCOPE

1. Primarily to enable freezing-point determinations to be accurately made on milk and other fluids within a short time.

2. To eliminate the inconveniences and annoyances attending the uses of ordinary laboratory apparatus.

3. To economize in the cost of freezing material.

4. To provide for accurate control of the temperature of the freezing bath.

Besides its use for determining the amount of water added to milk, the Hortvet Cryoscope has been recommended for determining the character of soil and sugar solutions, the freezing-point of oils, etc.

EIMER & AMEND

FOUNDED 1851

NEW YORK
3rd Ave., 18th to 19th St.

PITTSBURGH BRANCH
2011 Jenkins Arcade

Made in Italy

08-15 STD

8 082919 991409

www.colibrisystem.com

UNIVERSITY OF ILLINOIS-URBANA
3 0112 121400169